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USE OF SOIL PARAMETERS FOR DESCRIBING PESTICIDE MOVEMENT THROUGH SOILS

OKLAHOMA STATE UNIVERSITY

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Experimental results from laboratory and field studies were used to test the numerical solutions for their ability to describe the movement and distribution of pesticides in a soil profile with time. Equilibrium adsorption and desorption isotherms were not single-valued relationships in any of the soil-herbicide systems studied. Kinetic adsorption-desorption models were evaluated and shown to be inadequate for predicting herbicide mobility at high average pore-water velocities. An empirical model was developed, based on experimental data, and used to describe herbicide movement at high flow rates. The procedure defined a fraction of the soil adsorbing sites that were in equilibrium with the herbicide during displacement. This fraction was a function of the average pore-water velocity.

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By

J. M. Davidson
G. H. Brusewitz
D. R. Baker
A. L. Wood

Oklahoma State University
Stillwater, Oklahoma 74074

Project No. R-800364
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Project Officer

Dr. George W. Bailey
Southeast Environmental Research Laboratory
National Environmental Research Center
Athens, Georgia 30601

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ABSTRACT

Solutions of a differential equation for solute transport are described for both transient and steady state soil water conditions. The solutions use independently measured soil and soil-pesticide adsorption-desorption characteristics to describe the movement of a pesticide in a soil profile. Owing to the complexity of the soil-pesticide adsorption-desorption characteristics, numerical solutions of the soil water flow and solute transport equations were used. Numerical dispersion in the finite difference solution of the solute transport equation was considered and a correction included in the solution.

Experimental results from laboratory and field studies were used to test the numerical solutions for their ability to describe the movement and distribution of pesticides in a soil profile with time. ^{14}C-labeled herbicides were used in the laboratory experiments. Equilibrium adsorption and desorption isotherms were not single-valued relationships in any of the soil-herbicide systems studied. Kinetic adsorption-desorption models were evaluated and shown to be inadequate for predicting herbicide mobility at high average pore-water velocities. An empirical model was developed, based on experimental data, and used to describe herbicide movement at high flow rates. The procedure defined a fraction of the soil adsorbing sites that were in equilibrium with the herbicide during displacement. This fraction was a function of the average pore-water velocity. Using this empirical model, the distribution of a herbicide in a soil during infiltration was adequately described with the soil-water and solute transport equations.

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SECTION I

CONCLUSIONS

Numerous laboratory and field studies were used to evaluate the various parameters influencing the mobility of a herbicide in the soil. These data were then used to test existing mathematical models for their ability to describe the movement and distribution of selected herbicides in a soil profile with time. Based on these studies, several conclusions can be drawn.

1. Analytic solutions of a transport model frequently used in chromatography work were not adequate since they generally required various simplifying assumptions that were not characteristic of the soil-water-herbicide system. Also, the boundary conditions for which the solution was valid could not be maintained for extended periods of time under natural field conditions.

2. The adsorption and desorption isotherms for all herbicide soil systems studied were not single-valued functions. Excluding this nonsingularity when calculating the herbicide distribution in a soil resulted in a serious disagreement between the calculated and observed distributions. The experimental herbicide distributions were significantly wider and the maximum concentrations lower owing to the nonsignularity. Both laboratory and field results suggest the possibility of the herbicide being irreversibly adsorbed to the soil.

3. Kinetic adsorption-desorption models were evaluated and found inadequate for predicting herbicide mobility at high average pore-water

velocities. These models, however, agreed with the equilibrium Freundlich adsorption model when describing herbicide distributions at low pore-water velocities. The kinetic rate coefficients were difficult to measure and unless measured independently, could be selected on the basis of data fitting and thus erroneously include the spreading owing to hydrodynamic dispersion.

4. The herbicides studies appeared to be in equilibrium with some fraction of the soil mass when displaced through the soil at high pore-water velocities. An empirical model was used to describe the movement of several herbicides at high flow rates. The procedure defines a fraction of the adsorbing sites that were in equilibrium with the herbicide during the displacement. The fraction was a function of the average pore-water velocity. The procedure provides a reasonable fit between data and calculated distributions for large flow rates. Adsorption appears to be diffusion controlled as well as a function of pore geometry and pore size distribution.

5. Numerical solutions of the water and solute transport equations were solved simultaneously in order to describe herbicide movement during infiltration and soil water redistribution. The calculated and experimental (laboratory and field) values were in good agreement for several infiltration and redistribution studies. Equilibrium adsorption was assumed, but the parameters for adsorption and desorption could be the same or different for each process. Hydrodynamic dispersion was also considered and included in the solution.

6. Numerical dispersion in the finite difference solution of the solute transport equation was considered and a correction included. The solution, with a correction for numerical dispersion, was within 5% of an analytical solution. A single-valued adsorption-desoprtion function was used for the evaluation.

7. Fluometuron losses in the runoff under simulated rainfall conditions

were less than 0.5% of the total amount of chemical applied to the dry soil. Losses were highest when the herbicide was applied to a wet rather than a dry soil. The highest fluometuron losses occurred in the first runoff producing rainfall event after herbicide application.

8. The quantity of fluometuron on a gram of sediment was greater than that in an equal quantity of water. Because of the large dilution in the runoff, irreversible adsorption must be considered as well as the nonsingularity between adsorption and desorption.

SECTION II

RECOMMENDATIONS

The results of this study illustrate the feasibility of predicting the movement and distribution of herbicides under natural field conditions. The numerical solutions, in principle, could also be used to describe the behavior of other soluble components present in or applied to a soil, e.g., the movement of nitrogen and phosphorus. Since the water and solute transport equations were solved simultaneously, the suitability of the model to describe the transport processes at the soil surface (0-5 cm) should be experimentally evaluated.

Soil-pore geometry and size distribution appear to be major parameters not presently considered in the solute transport model. The importance of these soil physical properties to the adsorption process during solute movement through a soil need to be studied in detail. A diffusion controlled adsorption process is indicated by the present data. Experiments which will identify the parameters and define a model to describe the adsorption of pesticides at high flow rates should be conducted.

The nonsingularity between adsorption and desorption of herbicides has been well documented. However, to date these experiments have been confined to 1:1 (water to soil) batch experiments involving only one adsorption and desorption cycle. Under natural field conditions, the soil to water ratio varies and several adsorption-desorption cycles may occur within a short period of time. The adsorption-desorption process needs to be studied under more general environmental conditions. This type of information is necessary for any continuous simulation of herbicide movement and distribution in the soil.

Biological degradation submodels need to be developed and added to the solute transport model. These processes are significant in the soil surface region where the biomass is sensitive to temperature and water fluctuations. These models are also necessary for a continuous simulation of a biodegradable solute during the growing season. This information can be used to describe the attenuation of a soil applied pesticide with time.

SECTION III

INTRODUCTION

The use of pesticides in agricultural production programs has increased over the past several years. These chemicals have contributed to increased crop yields and in many cases, lower production costs. However, the effects of these chemicals are not always beneficial. In some instances, crop injury or failure has occurred because of herbicide residues from a previous cropping system. Environmental contamination is also a possibility that must be considered with the widespread use of pesticides. Some of these chemicals are also toxic to man and have undesirable effects on certain ecosystems (e.g.) biological magnification. Therefore, the agricultural producer as well as the environmentalist is concerned with the fate of a pesticide in a soil profile. Compounds of particular interest are those that are nonvolatile and biologically stable. These pesticides present a particular problem in that they may leave the target area on sediment and in the water flowing across and/or through the soil. The distribution of a pesticide with time within a soil profile depends upon its interaction (adsorption-desorption) with the soil matrix and the rate and direction of soil water movement.

Several mathematical models for describing the movement of an adsorbed chemical through a soil have been proposed[1 2 3 4] and tested[5 6 7 8 9 10] In general, the analytical solutions of these models, subject to rigid initial and boundary conditions, have been accepted without adequate validation. Many of the solutions are based upon assumptions which over-simplify the soil-water system and adsorption-desorption characteristics of the solute. For example, Hashimoto et al.[1] and Lapidus and Amundson[2] assumed pointwise equilibrium adsorption; whereas, the solutions of Lindstrom et al.[3] and Oddson et al.[4] used a kinetic adsorption model but assumed diffusion and dispersion to be negligible. Also, each of the models required the adsorption and desorption process to be a single-valued function; whereas, experimental data[7 11] have shown a nonsingular relationship to exist for several herbicide soil systems. Thus, it appears that the problem is too complex to obtain any analytical solution of the differential equations currently being used to describe both the transport and adsorption-desorption processes. The above models also require steady state soil water conditions.

The simultaneous transfer of water and solutes through a natural field soil occur generally as a transient process. The direction and rate at which each of the phases move are dependent upon the physical characteristics of the soil, climatic conditions, activity of the plant and biological system and interactions between the solute and soil matrix. An understanding of how these processes influence the transfer of each phase is essential in the development of management practices for minimum contamination to soil and/or water supplies. Numerical techniques to simulate the transient behavior of water and noninteracting solutes have been described by Bresler and Hanks[12], Bresler[13], and Kirda et al.[14] However, a numerical solution has not been developed and tested for the simultaneous transfer of water and adsorbed solutes in a soil.

In this study, a numerical simulation procedure for describing the simultaneous transport of water and adsorbed and nonadsorbed solutes was developed and evaluated. The combined effect of convection, adsorption-desorption, and dispersion (diffusion and mechanical dispersion) were considered as well as a correction for numerical dispersion in the finite difference solution of the solute transport equation. Experimental laboratory and field data were used to evaluate the suitability of the two numerical solutions to describe the movement of each phase. Adsorption and desorption was also studied for several herbicide-soil systems. Several adsorption models were considered and evaluated in the solute transport equation.

SECTION IV

THEORY

The basic equations used to describe the movement of a pesticide in a soil with isothermal conditions will be presented and discussed. Pesticide transport in the presence of both steady state and transient soil water conditions will be considered. Computer programs (FORTRAN IV), flow charts and input-output data formats for the numerical solution of the chemical and chemical plus soil water transport equations are presented in Appendix A and B, respectively. All symbols used in this manuscript are defined in the Glossary.

EQUATIONS FOR WATER FLOW

Darcy's equation was assumed to describe the flow of water in a saturated and/or unsaturated soil. The equation for flow in one dimension in an isotropic soil is

$$q = -K_{(\theta)} \frac{\partial \phi}{\partial z} \qquad (1)$$

where q = volumetric soil-water flux (cm/hr)

$K_{(\theta)}$ = hydraulic conductivity (cm/hr) which is a function of the soil water content θ (cm^3/cm^3)

ϕ = hydraulic head (cm)

z = soil depth (cm) measured positive downward

The volumetric soil-water flux is smaller in magnitude than the velocity of the water moving through the tortuous pore sequences. The average pore-water velocity is obtained by dividing the soil-water flux by the volumetric soil-water fraction.

Equation (1) describes a steady state soil water condition. Using equation (1) in the continuity equation (conservation of mass) gives the basic equation used to describe the transient flow of water through soils. The equation for one-dimensional flow is

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial z}\left[K_{(\theta)}\ \frac{\partial h}{\partial z} - K_{(\theta)}\right] \qquad (2)$$

where θ = volumetric water fraction (cm^3/cm^3)

t = time (hr)

h = soil water pressure head (cm)

The implicit finite difference analog of equation (2) for pressure head is

$$\frac{h_i^j - h_i^{j-1}}{\Delta t} = K_{i-\frac{1}{2}}^{j-\frac{1}{2}}\left[\frac{h_{i-1}^{j-1} + h_{i-1}^{j} + 2\Delta z - h_i^{j-1} - h_i^j}{2\Delta z^2\ Q_i^{j-\frac{1}{2}}}\right] - K_{i+\frac{1}{2}}^{j-\frac{1}{2}}\left[\frac{h_i^{j-1} + h_i^{j} + 2\Delta z - h_{i+1}^{j-1} - h_{i+1}^j}{2\Delta z^2\ Q_i^{j-\frac{1}{2}}}\right] \qquad (3)$$

where $Q_i^{j-\frac{1}{2}} = (\partial\theta/\partial h)_i^{j-\frac{1}{2}}$

i = space or depth indice

j = time indice

Equation (3) is solved using a similar procedure to that described by Hanks and Bowers[15]. The relationships between K and θ and h and θ are stored in the computer in a matrix and once h_i^j has been calculated, θ_i^j and K_i^j are obtained from the matrix.

The time increment, Δt, in equation (3) is variable and dependent upon the water infiltration and redistribution rate. The increment Δt^{j-1} used to calculate h_i^j during infiltration is obtained from

$$\Delta t^{j-1} = \frac{\Delta t^o I^o}{I^{j-1}} \qquad (4)$$

where Δt^o = selected time increment for $t = 0$

I^o = infiltration rate at $t = 2\Delta t^o$

The infiltration rate is obtained by using Darcy's equation. When evaporation at the soil surface and redistribution occur simultaneously within the profile, the time increment is obtained from

$$\Delta t^{j-1} = \frac{\Delta t_m K_m}{K_{max}^{j-1}} \tag{5}$$

where K_m = maximum hydraulic conductivity at cessation of infiltration

Δt_m = time increment at cessation of infiltration

K_{max}^{j-1} = maximum hydraulic conductivity in soil profile at j-1 time after the initiation of evaporation and/or redistribution of water

The computer algorithms (FORTRAN IV), flow chart and input-output data format are in Appendix B as part of the Hybrid solution for the simultaneous movement of water and solute.

The numerical solution of equation (3) will accept any initial distribution of θ and h with depth. The three physical cases considered in the program are: 1) constant θ_o^j and h_o^j at $z = 0$ for duration of infiltration; (2) constant water flux or any known water flux distribution which can be approximated as a series of constant fluxs with time at $x = 0$; and 3) evaporation (constant or variable with time) from the soil surface. Hysteresis in the θ and h relationship was not considered, but could be included using a procedure similar to that described by Rubin[16] and Stable[17].

The soil water flux and average pore-water velocity in each Δz increment of soil is calculated using equation (1). The parameters are obtained from equation (2) for each time increment and the matrix of h versus θ and K versus θ. Soil water flow rate and soil water content data are required in the pesticide transport equations described in the following sections.

EQUATIONS FOR ADSORPTION-DESORPTION

The distance an organic pesticide will move through a soil profile per unit of time is significantly influenced by the intermittent capture and release of the individual pesticide molecules by the soil matrix. The average time required for this adsorption or desorption to occur is dependent upon the free energy of activation required for each process. Adsorption and desorption may also be influenced by diffusion rate; where the capture and release occur gradually as the molecules diffuse in and out of the region of adsorption.

Adsorption and desorption in a one-site system (one adsorption-desorption mechanism) may be represented by the following model

$$C \underset{k_D}{\overset{k_A}{\rightleftharpoons}} \text{S-Adsorbent} \tag{6}$$

where k_A = adsorption rate coefficient (hr^{-1})
k_D = desorption rate coefficient (hr^{-1})
C = pesticide solution concentration ($\mu g/cm^3$)
S = adsorbed pesticide concentration ($\mu g/g$)

The rate of mass transfer to the adsorbed phase can be expressed as

$$\frac{dS}{dt} = \frac{k_A \theta C^{1/N}}{\rho} - k_D S = k_D \left[\frac{k_A \theta C^{1/N}}{k_D \rho} - S \right] \tag{7}$$

where ρ = bulk density of the soil system (g/cm^3)
N = constant that varies with pesticide and adsorbent

The other terms have been described previously and are in the Glossary. This same relation was used by Lapidus and Amundson[2] (for $N = 1$) to represent nonequilibrium adsorption and is similar in form to the adsorption model used by Oddson et al.[4] (for $N = 1$) and van Genuchten et al.[10]

Based upon the Arrhenius equation, the adsorption and desorption rate coefficients are temperature dependent and proportional to the free energies of activation for adsorption and desorption

$$k_A = k_A' \exp -\Delta G_A \dagger/RT \tag{8a}$$

$$k_D = k_D' \exp -\Delta G_D \dagger/RT \tag{8b}$$

where k_A' = constant generally referred to as frequency factor for adsorption
k_D' = constant generally referred to as frequency factor for desorption
$\Delta G_A\dagger$ = free energy of activation for adsorption
$\Delta G_D\dagger$ = free energy of activation for desorption
R = gas constant
T = absolute temperature

Fava and Eyring[18] and Lindstrom et al.[19] present a more complex adsorption model than that of equation (7) by allowing the activation energies for adsorption and desorption to change with surface coverage. Equation (7) assumes that the adsorption-desorption process is a single-valued function and that a linear relationship exists between S and C at equilibrium ($\partial S/\partial t = 0$) when N is unity. The coefficient k_A/k_D is constant for a specific soil and pesticide and is frequently referred to as a partition coefficient.[19]

A solution to equation (7) can be obtained by using Laplace transforms. For initial conditions of $C_{(o)}$ and $S_{(o)}$ equal to zero, the solution of equation (7) for $N = 1$ is

$$S_{(t)} = \frac{\theta k_A}{\rho} \int_o^t C(\tau) \exp[-k_D(t-\tau)]d\tau \tag{9}$$

where τ = variable of intergration

Note that the adsorbed concentration is an exponential function of time. The Freundlich equation has been shown by several investigators[20 21 22] to describe the relationship between the solution and adsorbed concentrations. The Freundlich equation is

$$S = K_A C^{1/N} \tag{10}$$

where K_A = adsorption distribution coefficient ($\mu g^{[1-1/N]} cm^{3/N} gm^{-1}$)
For equilibrium adsorption conditions, equations (7) and (10) are equal with $K_A = k_A\theta/k_D\rho$. Van Genuchten et al.[10] have used equations (7) and (10) in a solute transport equation to describe adsorption in a flowing system.

The adsorption-desorption phenomenon is generally assumed to be a single-valued function for isothermal conditions. The results of Davidson and McDougal[21] and Swanson and Dutt[11], however, indicate that adsorption and desorption were not single-valued functions for all herbicide-soil systems. For equilibrium desorption, more herbicide was retained on the soil at a given solution concentration than during adsorption. Rewriting equation (10) for desorption gives

$$S' = K_D C'^{1/N} \tag{11}$$

where prime (') = desorption

K_D = desorption distribution coefficient ($\mu g^{[1-1/N']} cm^{3/N'} gm^{-1}$)

When the adsorption process ceases, the solution and adsorbed concentrations in equations (10) and (11) are equal ($C = C'$ and $S = S'$). At this point, the solution concentration is a maximum (C_{max}). Setting equation (10) equal to equation (11) (S_{max}) = S'_{max}) and solving for K_D (C_{max} = C'_{max}) gives

$$K_D = K_A\, C_{max}^{(1/N - 1/N')} \tag{12}$$

where C_{max} = maximum pesticide solution concentration prior to desorption ($\mu g/cm^3$)

S_{max} = maximum adsorbed pesticide concentration prior to desorption ($\mu g/g$)

Note that the desorption distribution coefficient K_D is not constant, but a function of the maximum solution concentration at the time desorption was iniated. Also, the desorption distribution coefficient may exceed the adsorption distribution coefficient, depending upon the amount of chemical in solution prior to desorption. Equation (12) assumes N' is not a function of the maximum solution concentration; however, van Genuchten et al.[10] have shown that N' was inversely related to C_{max}, but could be assumed constant in many instances without serious error.

EQUATIONS FOR PESTICIDE TRANSPORT

The mass transport of a pesticide through soil in one dimension is generally assumed to be governed by convection (viscous movement of the soil water), diffusion (thermal motion of the pesticide within the soil water), mechanical dispersion (mixing owing to pore water velocity distribution) and adsorption-desorption. The partial differential equation frequently used to describe the miscible displacement of a pesticide for transient soil water flow conditions is

$$\frac{\partial(\theta C)}{\partial t} = \frac{\partial}{\partial z}\left[\theta D \frac{\partial C}{\partial z}\right] - \frac{\partial(qC)}{\partial z} - \rho\frac{\partial S}{\partial t} \qquad (13)$$

where D = apparent diffusion or dispersion coefficient (cm^2/hr)

Assuming D is independent of z and using the equation of continuity for water (Warrick et al.[23]) and equations (10) and (11), equation (13) becomes

$$\frac{\partial C}{\partial t} = \frac{D}{W}\frac{\partial^2 C}{\partial z^2} + \frac{1}{W}\left[\frac{D}{\theta}\frac{\partial \theta}{\partial z} - \frac{q}{\theta}\right]\frac{\partial C}{\partial z} \qquad (14)$$

where $W = 1 + \frac{\rho}{\theta N} K_A C^{(1/N-1)}$ for adsorption (15a)

$W = 1 + \frac{\rho}{\theta N'} K_D C'^{(1/N'-1)}$ for desorption (15b)

Based upon the work of van Genuchten et al.[10] and Hornsby and Davidson[7], the equilibrium Freundlich adsorption model appears adequate for most transient systems. The adsorption distribution coefficients can be measured independently using standard batch procedures[21]; whereas, the adsorption and desorption rate coefficients are difficult to measure.

The numerical solution of equation (14), for steady state soil water condition, using an explicit procedure of the finite difference scheme is

$$C_i^j = C_i^{j-1} + \frac{\Delta t}{W_i^{j-1}} D \left[\frac{C_{i+1}^{j-1} - 2C_i^{j-1} + C_{i-1}^{j-1}}{z^2} \right] - \frac{\Delta t\, q}{W_i^{j-1}\theta} \left[\frac{C_i^{j-1} - C_{i-1}^{j-1}}{\Delta z} \right] \qquad (16)$$

Numerical solutions by finite difference are subject to serious numerical dispersion (smearing of the concentration distribution) unless the time and spatial increments, Δt and Δz, for both $\partial C/\partial t$ and $\partial C/\partial z$ approach zero. To correct for numerical dispersion, a procedure similar to that described by Chaudhari[24] and Bresler[13] for a nonadsorbed solute ($W = 1$) was used. To approximate $\partial C/\partial t$ and $\partial C/\partial z$, $C_{(z,t)}$ is expanded about $t + \Delta t$ and $z - \Delta z$ using a Taylor series, only the first and second order terms from the expansions are retained. Expanding $C_{(z,t)}$ about t using a Taylor series gives

$$C(t + \Delta t) = C(t) + \left[\frac{D}{W} \frac{\partial^2 C}{\partial z^2} - \frac{q}{\theta W} \frac{\partial C}{\partial z} \right] \Delta t + \frac{\partial}{\partial t} \left[\frac{D}{W} \frac{\partial^2 C}{\partial z^2} - \frac{q}{\theta W} \frac{\partial C}{\partial z} \right] \frac{\Delta t^2}{2} + \ldots\ldots\ldots\ldots \qquad (17)$$

Using the chain rule and equations (14) and (15a), equation (17) becomes

$$C_{(t+\Delta t)} = C_{(t)} + \left[\frac{D}{W} \frac{\partial^2 C}{\partial z^2} - \frac{q}{\theta W} \frac{\partial C}{\partial z} \right] \Delta t - \left[\frac{D^2}{W^3} \frac{\rho}{\theta} \frac{K}{N} A^{(1/N-1)} \left(\frac{\partial^2 C}{\partial z^2} \right)^2 + \frac{q\rho}{W^3\theta^2} \frac{K}{N} A^{(1/N-1)} \left(\frac{\partial C}{\partial z} \right)^2 - \frac{q^2}{W^2\theta^2} \frac{\partial^2 C}{\partial z^2} + \frac{q^2\rho}{W^3\theta^3} \frac{K}{N} A^{(1/N-1)} \left(\frac{\partial C}{\partial z} \right)^2 \right] \frac{\Delta t^2}{2} \qquad (18)$$

Since $1/N$ for most herbicide soil-systems is close to unity, $(\partial^2 C/\partial z^2)^2$ $1/N(\frac{1}{N} - 1)$ can be assumed to be negligible and equation (18) reduced to

$$C(t+\Delta t) = C_{(t)} + \left[\frac{D\Delta t}{W} + \frac{q^2 \Delta t^2}{2\theta^2 W^2} \right] \frac{\partial^2 C}{\partial z^2} - \frac{q\Delta t}{W\theta} \frac{\partial C}{\partial z} \qquad (19)$$

The numerical dispersion associated with $\partial c/\partial z$ and $\partial^2 C/\partial z^2$ is corrected for in a similar manner to that shown by Chaudhari[24] where $C_{(z,t)}$ was expanded in Taylor series about z-Δz. The approximate correction for numerical dispersion in solving equation (16) for a steady state soil water condition is

$$D_N = \frac{q}{2\theta}\left[\Delta z - \frac{q\Delta t}{\theta W}\right] \tag{20}$$

An accurate approximation of equation (13) for steady state soil water conditions may be obtained when equation (16) uses $D-D_N$ for the dispersion coefficient. The computer algorithms (FORTRAN IV), flow chart and input-output data formats for the solution of equation (16) with equation (20) are given in Appendix A.

The numerical solution of equation (14) for transient soil water conditions was also obtained using an explicit procedure of the finite difference scheme. However, owing to the large number of terms required to account for numerical dispersion introduced by $\partial C/\partial t$ (W is a function of both C and θ for the transient problem) in equation (14), the special case of $K_A = 0$ (W = 1) was assumed to account for the major portion of the error from this term in the finite difference solution. The solution to equation (14) with the correction for numerical dispersion is

$$C_i^j = C_i^{j-1} + \frac{\Delta t}{W_i^{j-1}}\left(D_i^j - \hat{D}_{N_i}^j\right)\left[\frac{C_{i+1}^{j-1} - 2C_i^{j-1} + C_{i-1}^{j-1}}{\Delta z^2}\right] - \frac{\Delta t}{W_i^{j-1}}\left[X_i^j - \frac{\Delta t}{2}G_i^j\right]\left[\frac{C_i^{j-1} - C_{i-1}^{j-1}}{\Delta z}\right] \tag{21}$$

with

$$X_i^j = \left(\frac{q}{\theta}\right)_i^j - \left(\frac{D}{\theta}\right)_i^j\left[\frac{\theta_{i+1}^j - \theta_{i-1}^j}{2\Delta z}\right] \tag{22a}$$

$$\hat{D}_{N_i}^j = \tfrac{1}{2}\left[X_i^j\Delta z - (X_i^j)^2\,\Delta t - G_i^j\,\frac{\Delta z\Delta t}{2}\right] \tag{22b}$$

$$G_i^j = \frac{1}{(\theta_i^j)^2}\left\{\left[\frac{-(q_i^j)^2}{\theta_i^j} - 2(D_i^j)^2\left(\frac{\theta_{i+1}^j - 2\theta_i^j + \theta_{i-1}^j}{\Delta z^2}\right) - 2D_i^j\left(\frac{q_{i+1}^j - q_{i-1}^j}{2\Delta z}\right) + \right.\right.$$

$$\frac{(D_i^j)^2}{\theta_i^j}\left(\frac{\theta_{i+1}^j-\theta_{i-1}^j}{2\Delta z}\right)^2\Biggr]\left[\frac{\theta_{i+1}^j-\theta_{i-1}^j}{2\Delta z}\right]\Biggr\} - 2\left(\frac{D}{\theta}\right)_i^j\left[\frac{q_{i+1}^j-2q_i^j+q_{i-1}^j}{\Delta z^2}\right] - \frac{q_i^j-q_i^{j-1}}{\theta_i^j\Delta t} \qquad (22c)$$

The G and $\hat{D}_N$ terms are for the special case of $K_A = 0$. The space increment, Δz, is the major source of numerical dispersion (see D_N and $\hat{D}_N$ in equations [20] and [22b]) since Δt is generally several orders of magnitude smaller. The products involving the time increment in equations (20) and (22b) are also, in general, significantly less than Δz even for high soil water flow rates during infiltration. The computer algorithms (FORTRAN IV), flow chart and input-output data formats for the simultaneous movement of water and pesticide are given in Appendix B.

Because equilibrium adsorption-desorption is assumed, the adsorbed concentration, S, in each Δz increment can be obtained using the calculated solution concentration (equations [16] or [21]) at that position and the corresponding adsorption or desorption distribution coefficient (equations [10] and [11]). The quantity of pesticide in each phase is then calculated for each computer print out.

The calculation of W for equations (16) and (21) using equations (15a) and (15b) proceeds as follows: At various locations in the soil, $z = z_i^j$, the pesticide solution concentration increases as the invading miscible pesticide front moves through the soil, reaches a maximum (C_{max}) and begins to decrease. Equation (15a) is used at z_i^j when the concentration is increasing, and equation (15b) is used when the solution concentration at a given position is decreasing. The calculation of K_D (equation [12]) is made for each z_i^j position when a decrease in solution concentration is first observed at that location, and once calculated, remains constant for that depth increment (see Appendix B).

The dispersion coefficient, D, in equation (13) is pore-water velocity dependent and increases monotonically with an increase in pore-water velocity. Kirda et al.[14] and Fried and Combarnous[25] have evaluated various relationships between the dispersion coefficient and flow velocity and molecular diffusion. The relationships studied were empirical, but did exhibit the fact that below some pore-water velocity, the contribution of molecular diffusion to mixing can be considered significant. The following empirical relation was observed for the range of soil water flow rates studied by Hornsby and Davidson[7] and van Genuchten et al.[10]

$$D = 0.08\,\frac{q}{\theta} + 0.02 \tag{23}$$

Equation (23) was used to estimate the dispersion coefficient for equations (16) and (21).

The following initial and boundary conditions were considered in the numerical solution of equations (16) and (21).

$$\begin{array}{llll}
C_i^o = 0 & z \geq 0 & t = 0 & (24a) \\
C_i^j = C_o & z = 0 & 0 \leq t \leq T & \\
\text{until } \int_o^z (\theta C + \rho S)dz = A & & & \\
D\frac{\partial C}{\partial z} - \frac{q}{\theta} C = 0 & z = 0 & t > T & \\
C_i^o = C_{(z)} & 0 \leq z \leq z_o & t = 0 & \\
S_i^o = S_{(z)} & & & (24b) \\
C_i^o = 0 & z > z_o & t = 0 & \\
D\frac{\partial C}{\partial z} - \frac{q}{\theta} C = 0 & z = 0 & t > 0 & \\
C_i^j = 0 & z \geq (\frac{q}{\Delta\theta})t & t > 0 &
\end{array}$$

where A = quantity of pesticide applied to the soil surface or introduce at $z = 0$

$(q/\Delta\theta)t$ = position of wetting front

$\Delta\theta$ = change in volumetric water content

Boundary condition (24a) simulates the case where a concentration C_o of soluble pesticide is entering the soil at $z = 0$ (C_o being equal to the maximum solubility of the pesticide in water) and continues to enter the soil until all the material at $z = 0$ for $t = 0$ is in the soil.

For a stable solution of equation (16) or (21) the following condition was used

$$\frac{(D-D_N)\Delta t}{\Delta z^2} \leq \tfrac{1}{2} \qquad (25)$$

Lindstrom et al.[3] have used this criterion for steady state soil water conditions and shown that it provides sufficient stability. However, an additional criterion was found to be necessary in the solution of equation (21) because of the mass transport term.

$$\frac{q}{\theta} - \frac{D}{\theta}\frac{\partial\theta}{\partial z} \quad \Delta t \leq \tfrac{1}{4} \qquad (26)$$

The Crank-Nicholsen implicit finite difference scheme used to approximate equation (2) is unconditionally stable for any Δt and Δz values selected when the hydraulic conductivity is constant. The stability conditions when K is a nonlinear function of θ have not been determined analytically to date.

The size of the Δz increment in equations (3), (16), and (21) was fixed, with Δz in equation (21) fixed at an integral multiple of the Δz of the water flow solution. The Δt of the solute equation was allowed to adjust itself at each time step according to equations (25) and (26) while the Δt of the water flow equation varied according to equations (4) and (5). Since the solute time increments and the water flow time increments were calculated independent of one another, the calculatations were allowed to proceed in the water flow equation until the calculated time was greater than or equal to the calculated time of the pesticide transport equation. When this condition occurs, the calculations of the solute equation were carried out until the pesticide equation time was greater than or equal to the water flow time, at which point, the water flow equation was again used and the cycle repeated. Calculations were carried out using an IBM 360/65 computer.

SECTION V

MATERIALS AND METHODS

LABORATORY EXPERIMENTS

Steady State Soil Water Studies

Soil from the surface 15 cm of a Norge loam profile was Ca-saturated using 0.5 N calcium acetate and washed with 0.01 N $CaSO_4$ until no acetate was detected. The physical and chemical properties of the soil used in this study are given in Table 1.

Table 1. PHYSICAL AND CHEMICAL CHARACTERISTICS OF NORGE LOAM SOIL

Soil	Aggregate size	pH	CEC	Exchangeable Ca	Organic matter
	mm		meq/100 g		%
Norge loam, calcium saturated	>2.0	6.6	9.2	7.1	1.7

Mechanical analysis: 46.0% sand, 37.5% silt, 16.4% clay

The soil was air dried to 0.015 g/g water content and then passed through a 2.0 mm sieve. The soil was packed into lucite columns 30 cm long and 7.65 cm inside diameter to an approximate bulk density of 1.5 g/cm^3. Fritted-glass plates were sealed to the ends of the column to hold the soil in place and allow the inflow solution to be quickly changed (Fig. 1). The dry soil was then saturated with 0.01 N $CaSO_4$ solution and inflow and outflow volumes measured until equal. The average pore-water velocity was controlled with a constant volume pump.

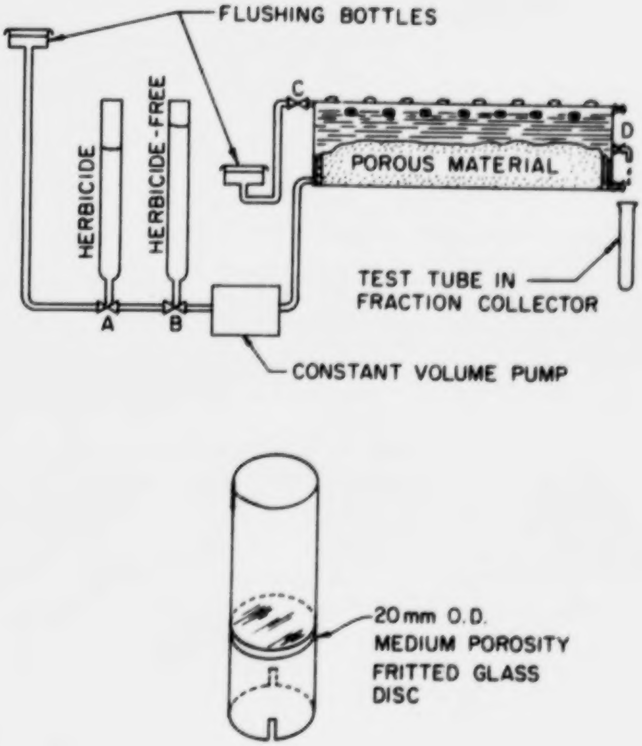
FLUSHING BOTTLES
C
D
HERBICIDE
HERBICIDE-FREE
POROUS MATERIAL
TEST TUBE IN FRACTION COLLECTOR
A
B
CONSTANT VOLUME PUMP
20mm O.D. MEDIUM POROSITY FRITTED GLASS DISC

Figure 1. Schematic drawing of apparatus used to study the displacement and distribution of fluometuron in Norge loam soil.

All studies were conducted at 25 ± 0.5 C.

A 200 ml pulse of ^{14}C-labeled 1, 1-dimethyl-3(α,α,α,-trifluor-m-tolyl) urea (fluometuron) in a 0.01 N $CaSO_4$ solution (5μc/l), equivalent to 1.11 kg/ha, was introduced at the inflow position and then displaced through the saturate soil with .01 N $CaSO_4$ at a constant flow rate. A total volume, including the 200 ml pulse, of 300, 600, and 900 ml of solution was added at each flow rate to replicate soil columns. When the desired throughput volume had been introduced, the flow process was stopped and saturated soil samples were taken immediately at 2 cm intervals along the soil columns. The samples were obtained from previously stoppered openings along the column (Fig. 1). These samples were used to determine the fluometuron solution and adsorbed concentration distribution at the time of sampling. Separation of the solution and adsorbed phases was accomplished by centrifuging the samples at 25 ± 1.0 C immediately after sampling using specially constructed fritted-glass filters (Fig. 1) at 1205 x G for 5 min. The solution sample obtained by this procedure was analyzed for ^{14}C activity and assumed to represent the solution concentration (μg/cm^3).

Extraction of the remaining herbicide from the soil was made using three successive 5 ml leachings with 95% ethyl alcohol. Preliminary studies revealed that an insignificant amount of fluometuron remained in the soil sample after three leachings. Since the initial centrifugation did not remove all the water from the sample, the fluometuron in the remaining solution had to be subtracted from the total concentration measured in the alcohol. This was determined by measuring the soil water content and knowing the solution concentration. The adsorbed concentration was expressed as (μg/g). It was assumed that the sampling and centrifugation were carried out rapidly enough to provide a true measure of the concentration of each phase.

Analyses of the soil solution and alcohol leachate for ^{14}C activity were made using a liquid scintillation technique. Duplicate 0.5 ml aliquots were pipetted into separate scintillation vials containing 15 ml of scintillation solution. The scintillation solution was composed of 120 g of napthalene, 4 g of 2,5-diphenyloxazole (PPO), and 50 mg of 1,4-bis-2- (5-phenyloxazolyl)-benzene (POPOP) made to 1 liter with p-dioxane. Preliminary studies revealed no difference in quenching due to varying the amount of ethyl alcohol or water in the sample aliquot. ^{14}C activity was used as a direct measure of the herbicide concentration.

In several studies, ^{14}C-labeled herbicide was displaced through the soil column and effluent samples analyzed for ^{14}C activity. Five milliters effluent water samples for herbicide analysis were collected sequentially with a fraction collector. The relative concentration (C/C_o) was calculated from the herbicide concentration in the effluent (C) and the original concentration (C_o) of the herbicide at the inflow location. At the completion of each herbicide displacement, the volume of water (V_O) held in the soil was determined gravimetrically. The number of pore volumes (V/V_O) displaced through the soil was calculated by dividing the volume of effluent (V) by the volumetric water capacity (V_o) of the soil.

Equilibrium adsorption-desorption isotherms were obtained by shaking duplicate samples of soil and herbicide solution (10 g soil to 10 ml solution) in screw-capped glass vials for 8 hours at 25 ± 0.5 C. The vials were centrifuged at 1250 x G for 5 min. at 25 ± 1.0 C and duplicate 0.5 ml aliquots of the supernatant were removed for analysis by liquid scintillation. For the desorption isotherm, 1.0 ml of 0.01 N $CaSO_4$ was added to replace the 1.0 ml sample removed for ^{14}C analysis. This dilution of the herbicide solution resulted in a desorption of the material from the soil matrix. The procedure was repeated to achieve successive dilutions of the herbicide solution. Blanks were run under identical conditions (soil deleted). Differences between blanks and samples containing soil were considered as the amount adsorbed or desorbed. All samples were run in duplicate.

Transient Soil Water Studies

The soil used in this study was obtained from the top 15 cm of a profile classified as Cobb fine sandy loam. The sampling site was located on the Caddo Research Station near Fort Cobb, Oklahoma. Based on the particle size distribution and for convenience, the sampled soil will be referred to as Cobb sand in this report. The soil was air-dried and passed through a 2.0 mm sieve. Gravimetric water content of the air-dry soil was 0.005 g/g. The pH, organic matter content and cation exchange capacity of the soil were 7.0, 0.5%, and 3.9 meq/100 g, respectively. The soil had 91.8% sand, 6.0% silt and 2.2% clay.

The air-dry soil was packed into rectangular acrylic columns one meter in length and having 13 by 13 cm inside dimensions. Soil was added to the column in 2 cm increments with each layer stirred into the top of the previous layer. After each soil addition, each side of the column was tapped four times with a rubber-faced mallet. This procedure was repeated until the total depth of soil reached 95 cm. The average bulk density of the soil in each column was 1.53 ± 0.015 g/cm^3.

The volumetric water content and initial bulk density at various locations along the length of the soil was measured by gamma-ray attenuation. The apparatus, Figure 2, consisted of a 250 millicurie Cesium-137 source, thallium-activated NaI crystal scintillation detector (Harshaw Type 4S4), and the following Harshaw electronic equipment: preamplifier (Model NB-11), linear amplifier (Model NA-11) single channel pulse height analyzer (Model NC-11), scaler (Model NS-30), timer (Model NT-29), and high voltage supply (Model NV-19). The scaler was coupled to a Hewlett Packard 5050B digital recorder. The system was found to have a resolving time and mass adsorption coefficients for water and soil of 3.3 microseconds, 0.0855 cm^2/g and 0.0797 cm^2/g, respectively.

A fluometuron concentration of 1.03 μg/ml in absolute ethanol was obtained by combining 80% wettable powder (technical grade) and ^{14}C-labeled fluometuron (100 μc/9.7 mg) in proper proportions to yield a ^{14}C activity of 0.556 μc/ml of solution. Three milliliters of this

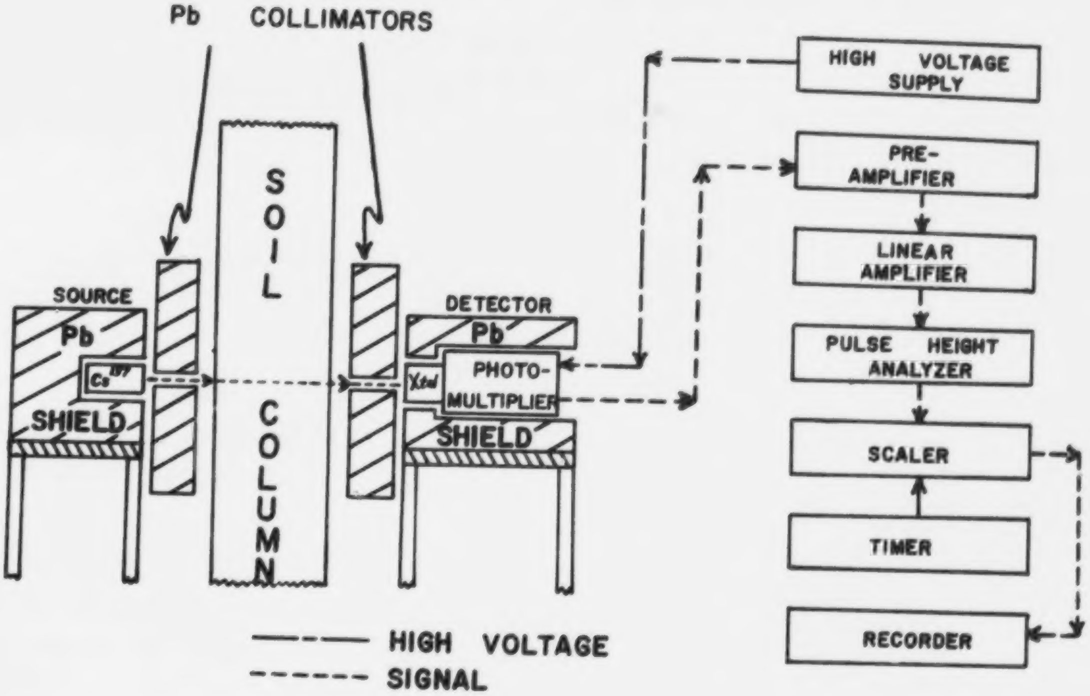
Pb COLLIMATORS
SOURCE
Pb
Cs137
SHIELD
SOIL
COLUMN
DETECTOR
Pb
Xtal
PHOTO-MULTIPLIER
SHIELD
HIGH VOLTAGE SUPPLY
PRE-AMPLIFIER
LINEAR AMPLIFIER
PULSE HEIGHT ANALYZER
SCALER
TIMER
RECORDER
HIGH VOLTAGE
SIGNAL

Figure 2. Schematic of gamma-ray attenuation apparatus.

solution were applied uniformly to the soil surface prior to initiating infiltration. This was equivalent to an application rate of 3.24 kg/ha. The soil surface was divided into three equal areas and the solution containing the fluometuron was added dropwise at random to each area with a 1 ml pipette. The ethanol was allowed to evaporate prior to the application of water.

After application of the herbicide, a 2 cm layer of 0.5-1.0 mm diameter quartz sand was placed on the soil surface. This was done to achieve a uniform distribution of water at the soil surface with the low infiltration rates and prevent puddling of the soil surface.

Constant infiltration rates of 1 or 5 cm/hr of 0.01 N $CaSO_4$ solution were obtained with a constant volume pump. The pump supplied water to a manifold with thirteen outlets. Each outlet was connected to a two-inch length of capillary tubing mounted in a 20 cm square acrylic plate, Figure 3. The capillary tubing had an inside diameter of 0.5 ± 0.25 mm. The plate was designed to fit on top of the acrylic columns containing the soil. The plate was moved over the soil surface from time to time to achieve complete coverage of the soil area. In order to monitor the rate of water addition, the 0.01 N $CaSO_4$ solution source was pumped from a flask positioned on a Mettler model P3 balance.

A one centimeter head of water was maintained on the soil surface when the infiltration rate was not controlled. Two four-liter Erlenmeyer flasks containing 0.01 N $CaSO_4$ solution were used to maintain this head. These flasks were mounted on platforms attached to the elevator of the gamma-ray attenuation apparatus. The flasks were weighed before and after infiltration to determine the total quantity of water that had entered the soil.

Samples of soil water were collected at various soil depths during infiltration through 10 mm fine-porosity fritted-glass immersion tubes. The tubes were located in the sides of the acrylic container beginning 5 cm below the soil surface and extending to 75 cm in 5 cm increments,

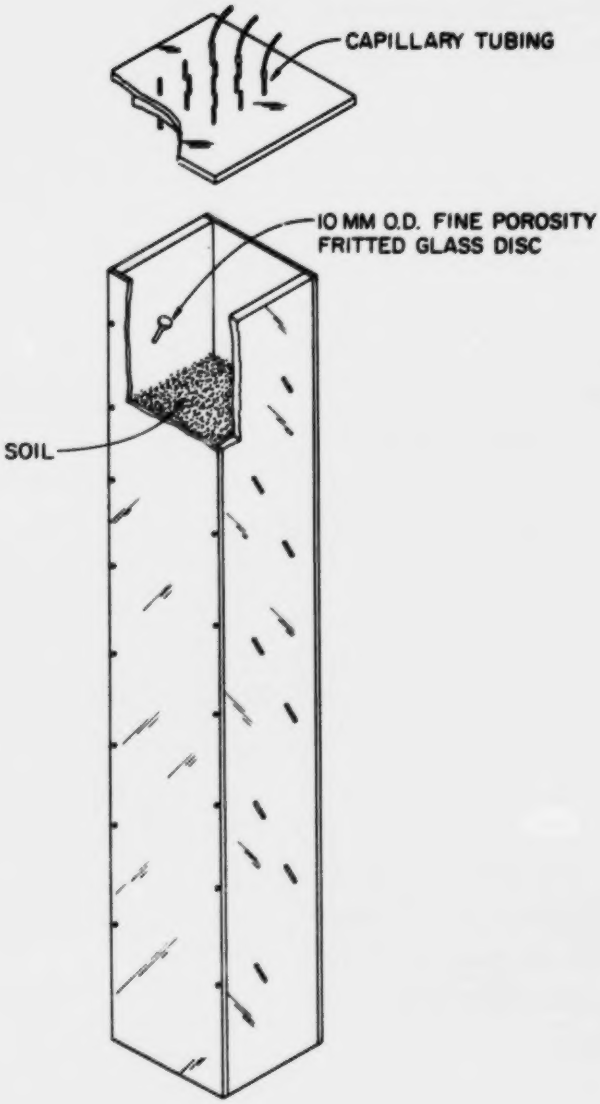
CAPILLARY TUBING
10 MM O.D. FINE POROSITY FRITTED GLASS DISC
SOIL

Figure 3. Soil column and water application apparatus used in transient soil water studies.

Figure 3. An additional tube was placed 2 cm below the soil surface. Rubber septums mounted on the open ends of the immersion tubes allowed soil solution samples to be drawn through the fritted discs. Glass syringes were used to draw samples from the soil after the wetting front had passed a given sampler. Herbicide concentration (^{14}C activity) in each soil water sample was measured by liquid scintillation. Immediately after cessation of infiltration, the column of soil was removed from the elevator associated with the gamma-ray attenuation apparatus. One side of the acrylic column was removed and the soil was sampled at three centimeter intervals beginning at the wetted front. The solution and adsorbed herbicide concentration in each core sample was determined using the procedure described in the steady state soil water studies section.

Soil moisture characteristics for Cobb sand packed to a density equal to that used in the soil columns were determined for both wetting and drying cycles. Soil cores 7.62 cm in diameter were placed on fritted glass plates in Buechner funnels. The soil was saturated for 24 hours and then allowed to drain to an equilibrium water content at a pressure of -4 cm of water. By increasing the air pressure in the Buechner funnels in given increments and measuring the quantity of water drained from the soil between these increments, a soil-water content pressure head relationship for the drainage cycle was obtained. When the soil reached equilibrium at the last pressure increment, a constant head burette was connected to the out flow end of the system. The pressure was then decreased by given increments and the amount of water flowing out of the burette and into the soil was measured. In this way, a soil-water content-pressure head relationship was determined for a wetting cycle. The pressure at which wetting was initiated was varied in order to obtain several soil water characteristic scanning curves for wetting.

Soil water diffusivities were determined with the method outlined by Bruce and Klute[26]. Water was applied to air-dry soil packed into a 3.1 cm diameter acrylic column. The pressure at the inflow end of the column was maintained at -2 cm. At the end of infiltration the column was sectioned into one centimeter segments and the water content of each segment was measured gravimetrically.

FIELD EXPERIMENTS

Runoff experiments were conducted in the field on a Teller sandy loam near Perkins, Oklahoma. The pH, cation exchange capacity, organic matter and clay content were 6.6, 7.3 meq/100 g, 1.2% and 20%, respectively. The average surface slope of the experimental area was 1%. Prior to construction of each runoff experimental plot, the area was plowed 15 cm deep and worked to obtain a good tilth. Cotton (Gossypium hirsutum L. 'Westburn 70') was seeded in rows 1.2 m apart the day the plots were constructed.

Individual runoff plots were 1.52 x 4.57 m in size with 1.52 m between plots. Each plot was arranged so that a row of cotton and its corresponding wheel track ran the full length of the center of the plot. Each plot was bordered with stainless steel edging that extended 12 cm below the soil surface. A sheet metal catchment device with an opening extending the full width of the plot was installed at the lower end of each plot. The opening of the catchment was hooded to prevent direct entry of rainfall. Runoff was transferred from the catchment to a stainless steel barrel for collection and sampling. After installation of the border and catchment, the plots were smoothed around the inside border. The planter furrow and wheel track in the plot were left intact. All field runoff experiments were repeated, but because of minor climatic variations that occurred between simulated rainfall events they were not considered replications.

Commercial fluometuron at 2.8 kg/ha was applied to the plots with a calibrated tractor sprayer in a water carrier volume of 374 L/ha. The spray boom extended across the plot, but the tractor was driven outside the plot. Immediately after the herbicide application, soil samples were taken from within the plot for initial herbicide concentration determinations. Soil samples for fluometuron content were taken from the 0-5 cm depth.

Rainfall was simulated with an oscillating lawn sprinkler that applied 1.2 cm of water per hour when operated continuously. This specific sprinkler was chosen for its uniformity of coverage and output.

In all runoff experiments, water was applied until a total of 45.5 L (approximately ¼ acre-inch) of runoff was obtained. A representative water sample was collected from the first 3.8 L of runoff, and another was collected from a composite of the next 41.6 L of runoff after thoroughly suspending the sediment. The amount of sediment in this sample was used to compute the total sediment loss from the plot. A sediment sample for fluometuron analysis was obtained by flocculating the suspended material in the composite runoff sample. All runoff samples were frozen until analysis.

The effect of rainfall intensity was studied by varying the time of water application. Three intensities were simulated - fast, intermediate, and slow: Fast, the water was applied at 1.2 cm/hr until runoff samples were obtained; intermediate, 0.6 cm increments of water were added over a three-hour period until 2.5 cm was applied, and then 1.2 cm/hr of water was applied until all runoff samples were obtained; slow 0.3 cm increments of water were added over a 4-day period until a total of 6.3 cm had been applied. No lateral runoff occurred from the slow treatment. Two days after each water application treatment, samples from the 0-5, 5-10, and 10-20 cm soil depths were taken from each plot to determine the extent of vertical fluometuron movement.

The effect of antecedent soil moisture on fluometuron movement was studied using "wet" and "dry" plots. The plot area was dried by tillage and then those plots designated dry were covered while those designated wet received 4.5 cm of simulated rainfall and then were allowed to dry for 24 hours. Fluometuron was then applied to all plots at a 2.2 kg/ha rate. Simulated rainfall (1.2 cm/hr) was applied until runoff samples were obtained. Soil samples were taken as described above.

Dissipation and vertical movement of fluometuron during the growing season was studied by sampling the soil in the rainfall intensity study at three dates over an 84-day period. The first sampling date was immediately subsequent to the first simulated runoff study. The sampling depths were 0-5, 5-10, 10-20, and 20-30 cm.

The chemical analytical method for fluometuron in soil and water was supplied by Ciba-Geigy, manufacturers of the herbicide. Bioassays were also conducted on the soil samples and a few selected water samples as an alternate analysis method. Soil samples were thawed, air dried, and screened to pass a 1 mm screen prior to analysis. Water samples were thawed and filtered.

For chemical assay, the fluometuron was hydrolyzed to 3-trifluoro-methyl aniline and extracted by steam distillation with isooctane. The extraced aniline was diazolized and coupled with N-ethyl-1-napthylamine to develop the color. The concentration of the herbicide was determined spectrophotometrically. The procedure was modified to eliminate the use of a clean-up column since the soil and water samples in this study did not produce a strong background color. The background from the untreated samples was substracted from the sample readings and the cleanup procedure was not needed. The basic procedure was as follows: using a 25 g soil sample or a 100 ml water sample, the fluometuron was extracted by distillation with isooctane, cooled, and the isooctane was extracted with 0.25 N HCl. Three extractions with 10 ml 1.0 N HCl were used and the final volume adjusted to 50 ml with 1.0 N HCl. The color was developed as outlined, and the colored HCl solution was extracted with a 20 ml N-butanol. The colored butanol extract was transferred to a test tube, and 10 g of anhydrous sodium sulfate granules were added. The colored extracts were quantified spectrophotometrically at 525 mμ.

Standards were prepared by spiking samples of water obtained from check plots with analytical fluometuron. The standard curve range was from 0.01 μg/ml to 0.6 μg/ml. Water samples and standards were read in a 4 cm lightpath cuvette. Soil standards for the chemical and bioassay analysis were prepared in a similar manner. The herbicide was added to soil in a volume of water sufficient to bring the soil to 10% water by weight. The samples were mixed, air dried and screened through a 1 mm screen. The standard curve was from 0.1 to 6.0 µg/g. Soil samples were read in a 1 cm cuvette. To determine the precision of the method, standard deviations were determined for six replicate samples at three different concentrations of fluometuron in soil and water. The absorbance values for fluometuron extracted from water or soil showed a linear response over the range of fluometuron concentrations found in all experiments. For the water analysis, the standard deviations were ± 0.002 at 0.05 µg/ml, ± 0.005 at 0.1 µg/ml, and ± 0.03 at 0.4 µg/ml. For the soil analysis, the standard deviations were < ± 0.01 at 0.04 g/g, ± 0.07 at 2 µg/g and ± 0.45 at 6 µg/g. Coefficients of variation were between 19 and 21% for all bioassay experiments.

Soil bioassays, using oats (*Avena sativa* L. 'Ciammaron'), were conducted in styrofoam cups. The soils were thoroughly mixed and 225 g of soil placed in each cup, planted, and subirrigated. The cups were placed under lights in a randomized block design with 4 replications. After 14 days, fresh weights of the oat tops were determined. The data were converted to µg/g using a standard curve. The standards were prepared as previously described. Water bioassays for fluometuron utilizing cucumber leaf disks were used as described by Truelove[27].

SECTION VI

RESULTS AND DISCUSSION

The numerical solution of equation (14) using the finite difference scheme described in equation (16) is compared with an exact or analytical solution (Davidson, et al.[28]) in Figure 4 for steady state soil water conditions. The initial and boundary conditions are described in equation (24a). The adsorption-desorption process was assumed to be linear and a single valued function, with K_A and K_D equal to 2.0 cm^3/g. The concentration at $z = 0$ was maintained at $C_o = 90\ \mu g/cm^3$ for 2.0 hours after which time it was reduced to zero. All other parameters necessary for the solution of equation (14) are given in Figure 4. The numerical dispersion associated with equation (16) for steady state soil water conditions was corrected for using the D_N term from equation (20). The agreement between the exact and numerical solution of equation (14) is reasonable (Figure 4). The general shape and position of the two relative concentration distributions are in good agreement; however, the numerical solution of equation (14) resulted in approximately 5% more area under the calculated values than under the exact solution (solid line). The correction for numerical dispersion was better when K_A was equal to zero, and agreed with the results reported by Bresler[13] for non-interacting solutes. An adsorption distribution coefficient, K_A, of 2.0 cm^3/g is large compared to that frequently measured in soil applied pesticide systems where the mobility of the pesticide presents a major or significant environmental problem. Thus, corrections for numerical dispersion using the relations in equation (20) for steady state soil water conditions should be adequate for those systems involving more mobile solutes ($K_A < 2.0\ cm^3/g$).

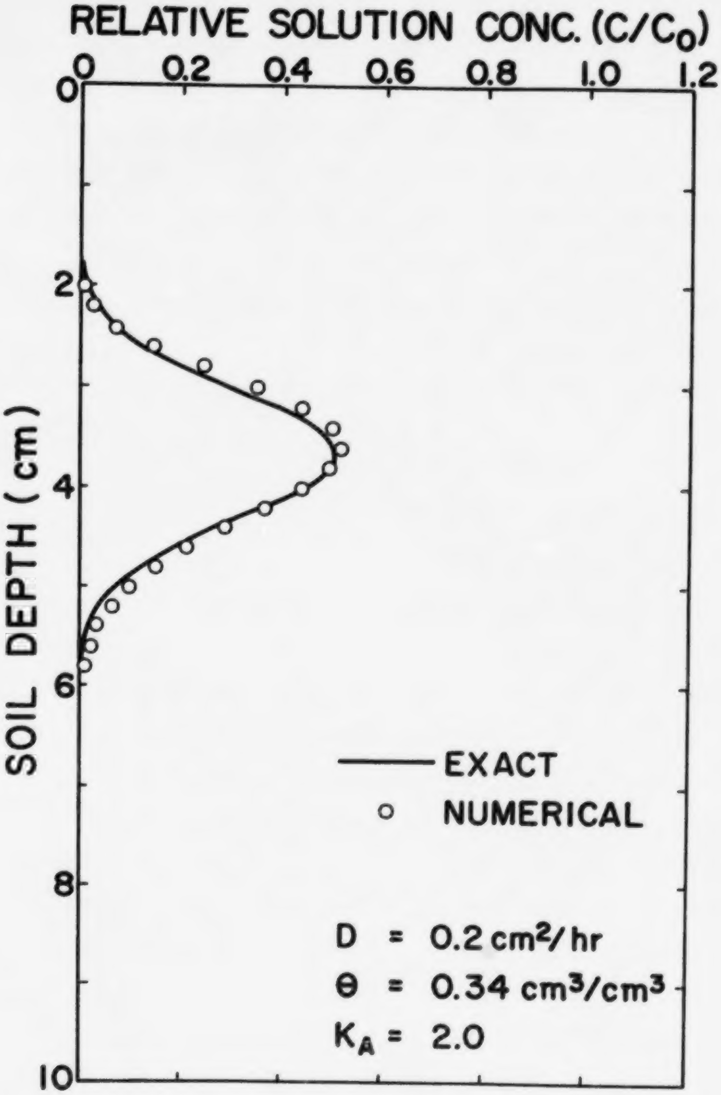

Figure 4. Computed relative solution concentration distribution using an exact and finite difference solution of equation (13). Calculations were made using an average pore-water velocity, dispersion coefficient, distribution coefficient and soil water content of 4.0 cm/hr, 0.2 cm^2/hr, 2.0 and 0.34 cm^3/cm^3, respectively.

The use of the numerical dispersion correction relations from equation (22) in equation (21) produces a very complex computer program. Figure (5) shows the agreement with G included (solid line) or excluded (open circles) from the simultaneous solution of equations (2) and (13) with $K_A = 0$. The initial soil water content was 0.12 cm^3/cm^3 and the pressure head at the soil surface ($z = 0$) was zero throughout the displacement. If K_A is not equal to zero, then the solute pulse is retarded and appears closer to the soil surface where the $\partial\theta/\partial z$, $\partial^2\theta/\partial z^2$, $\partial q/\partial z$ and $\partial^2 q/\partial z^2$ terms are more nearly equal to zero. The fact that the calculations for G included and G excluded agree so well for $K_A = 0$ under transient conditions (Figure 5) suggests that the term could be eliminated from the program for $K_A \geq 0$.

LABORATORY EXPERIMENTS

Steady State Soil Water Studies

Equilibrium adsorption and desorption isotherms for fluometuron and Norge loam soil are shown in Figure 6. Both processes are described reasonably well by the Freundlich equation (Equation 10). All lines are a least-squares fit with the correlation coefficient exceeding 0.98 for all lines. The adsorption isotherm is described by the equation given in Figure 6. Adsorption and desorption did not give a single-valued function. Similar results for adsorption and desorption have been reported by Swanson and Dutt[11] and van Genuchten et al.[10] Adsorption was 90% complete after 40 min of contact and equilibrium conditions existed after 120 min. Using the parameters determined for equilibrium adsorption, Figure 2, and the amount of herbicide adsorbed between 10 and 40 min, the desorption rate coefficient, k_D, was calculated (Equation 7) for each initial solution concentration studied. The average calculated rate coefficient was 3.5 $hour^{-1}$ and did not appear to be concentration dependent. Desorption rate coefficients were not calculated for times greater than 40 min owing to the difficulty of measuring small changes in adsorbed and solution concentrations with time.

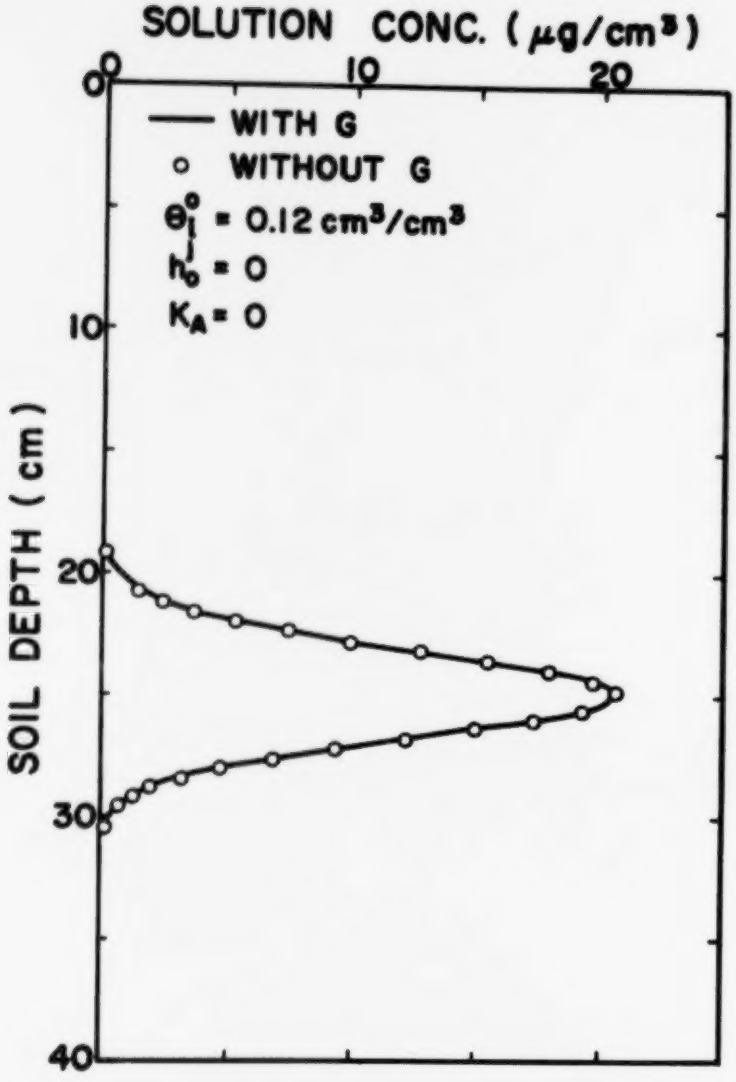

Figure 5. Computed solution concentration distribution of a non-adsorbed solute during infiltration with the numerical dispersion correction (equations [21] and [22]) for transient soil water conditions included and excluded.

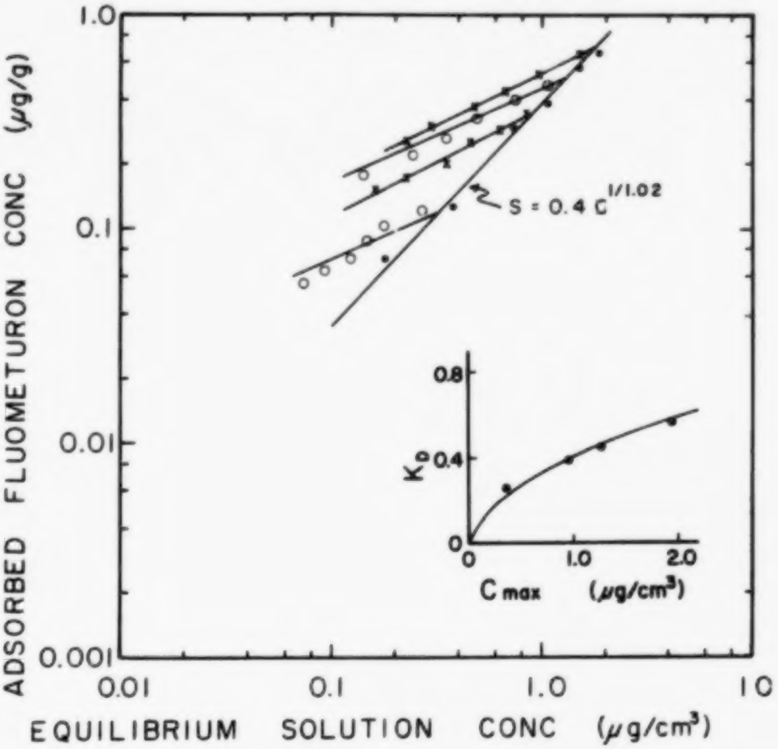

Figure 6. Equilibrium adsorption and desorption isotherms for fluometuron and Norge loam. Insert shows relationship between the desorption distribution coefficient, K_D, and the maximum fluometuron solution concentration, C_{max}.

The dependence of the desorption distribution coefficient upon the maximum fluometuron solution concentration is shown in Figure 6 (insert). The line was calculated using equation (12) and a N and N' of 1.02 and 2.30, respectively. The data points are the measured distribution coefficients and C_{max} from the desorption lines shown in Figure 6. The agreement is well within experimental error and justifies the use of a constant N' rather than the measured value that increases with a decrease in C_{max}.

Earlier studies using effluent data have shown that equilibrium adsorption may not exist at high soil-water flow rates [5 9]. Figure 7 gives the relative solution and adsorbed fluometuron concentrations at various locations in the soil following the introduction of 200 ml of fluometuron solution plus 100 ml of 0.01 N $CaSO_4$ solution (a total of approximately 0.64 pore volume) at two flow rates. The right hand portion of each "loop", for each flow rate, was obtained from the invading fluometuron front. The left hand part of the "loop" comes from the tailing edge or after a maximum concentration has moved past a given soil location. The presence of a nonsingular relationship between adsorption and desorption is shown by the fact that the adsorption and desorption data form a loop rather than a single-valued line. Also, the dependence of the adsorption upon the flow rate is illustrated by the right-hand shift of the fast flow rate data as well as the lower absorbed concentrations for a given solution concentration when compared with the slower displacement.

The adsorption data (Figure 7) from the slow displacement is similar to the equilibrium adsorption isotherm presented in Figure 6. Thus, for an average pore-water velocity of 0.59 cm/hour, equilibrium adsorption appears to exist between fluometuron and the Norge soil. For this case, the adsorbed and solution phases move together whereas as the high flow rate, the solution phase (peak concentration) will precede the adsorbed phase during displacement. Therefore, a greater spreading or flatter concentration distribution will exist[29].

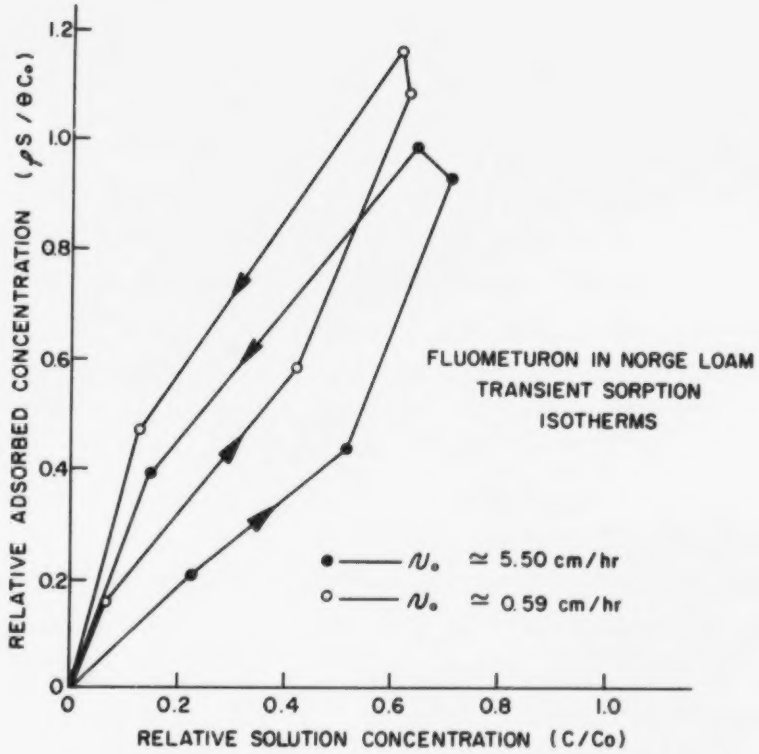

Figure 7. Transient adsorption-desorption behavior of fluometuron in Norge loam soil for 0.59 and 5.5 cm/hr average pore water velocity.

The relative solution and adsorbed concentration at 2 cm increments along the soil column for three displacement periods are given in Figures 8 and 9. The solid lines were obtained from the numerical solution of equation (13) using equation (10) for adsorption and desorption. The values of q/θ, K_A, N, N', and D were 0.59 cm/hr, 0.4, 1.02, 2.30, and 0.06 cm^2/ hour, respectively. Other physical data used to calculate the concentration distributions are given in Table 2.

Table 2. EXPERIMENTAL PARAMETERS FOR SOIL COLUMN STUDIED

Total throughput volume	Bulk density	Soil-water content	Solution flux	Pore-water velocity	Total time	Pore volume
cm^3	g/cm^3 (ρ)	cm^3/cm^3 (θ)	cm/hour	cm/hour (ν_0)	hour	cm^3
300	1.50	0.396	2.10	5.30	3.15	539
600	1.50	0.383	2.10	5.49	6.30	520
900	1.50	0.373	2.14	5.73	9.30	507
300	1.50	0.347	0.22	0.63	30.1	511
600	1.51	0.382	0.22	0.57	60.7	520
900	1.52	0.378	0.22	0.58	91.0	514

The dispersion coefficient, D, for fluometuron was assumed equal to that for chloride and was determined from chloride data (used the model proposed by Hashimoto et al.[1]). Reasonably good agreement was obtained between experimental and calculated relative solution and adsorbed concentration distributions (Figures 8 and 9). Note that the position of the peak concentration in Figures 8 and 9 occurs at the same location for each throughput volume indicating that the average pore-water velocity was low enough to permit equilibrium adsorption and desorption. Also, the tailing edge of the relative solution concentration is well described by the calculated line indicating that the desorption process was adequately defined by the model. Variations between measured and calculated values can be attributed, partially, to experimental error.

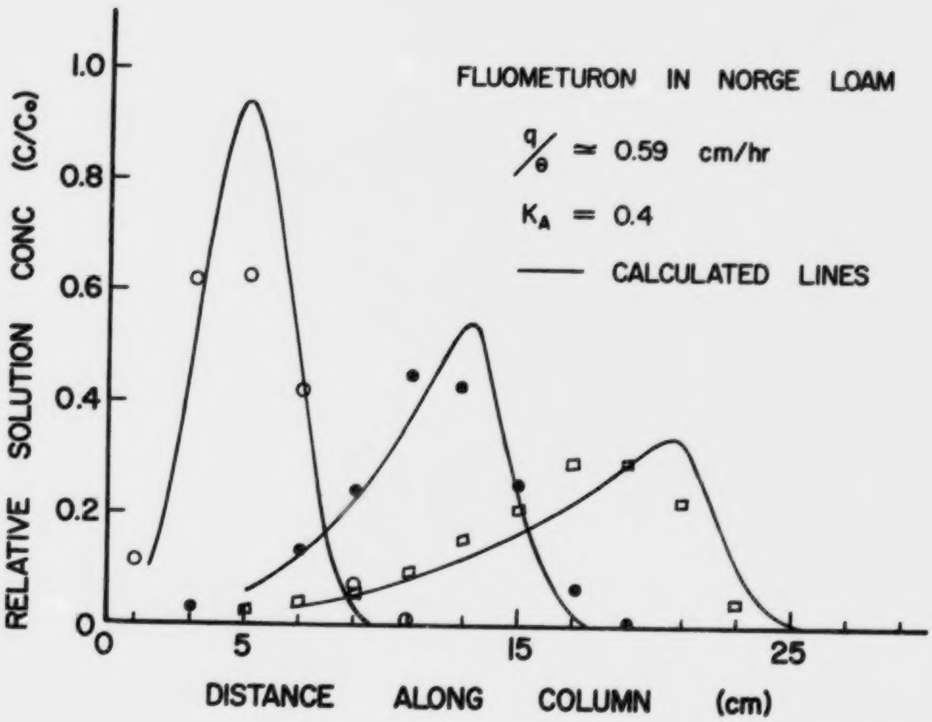

Figure 8. Calculated and experimental relative solution concentration distribution for 0.59 cm/hr average pore-water velocity. Calculated lines were obtained from a numerical solution of equation (14).

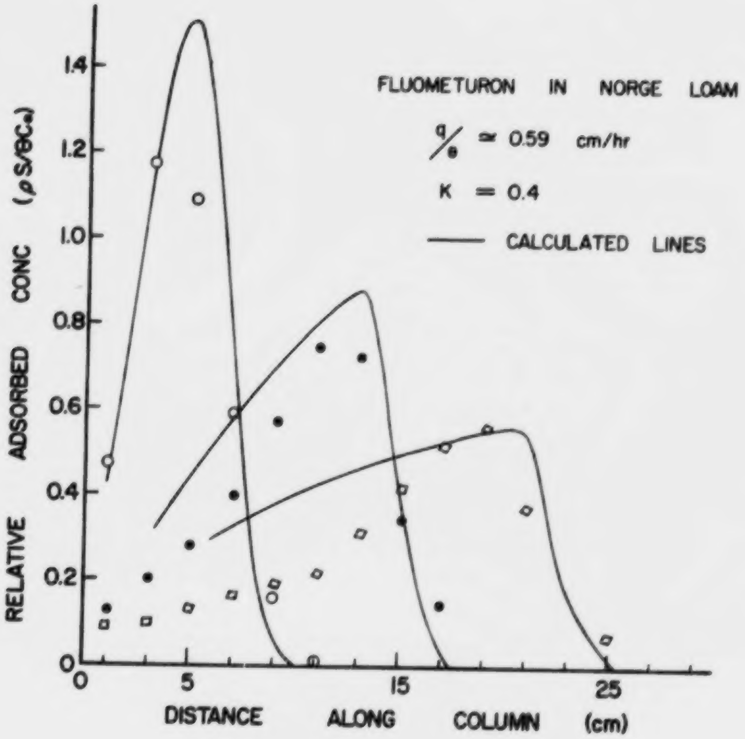

Figure 9. Calculated and experimental relative adsorbed concentration distribution for 0.59 cm/hr average pore-water velocity. Calculated lines were obtained from a numerical solution of equation (14).

Selecting a larger (2.8) or smaller (1.8) N' value did not significantly change the fit of the line to the data except in the maximum concentration region. Higher values of N' moved the peak concentration to the right and lowered the maximum concentration. The lower value of N' produced the opposite results.

Increasing the average pore-water velocity tenfold, while holding the throughput volumes constant, gives the solution and adsorbed concentration distributions shown in Figures 10 and 11. At this pore-water velocity (5.5 cm/hour), equilibrium adsorption does not exist at all locations within the soil mass (Figure 7). Therefore, the kinetics of the adsorption-desorption process would appear to be beneficial. However, the work of van Genuchten[10] with various kinetic models does not support this conclusion. Using the same adsorption-desorption parameters as those used for the slow flow rate (Table 2) and the numerical solution to equation (13), the relative solution and adsorbed fluometuron concentration distributions within the soil were calculated (Figures 10 and 11).

The maximum measured relative solution concentration occurs to the right of the measured relative adsorbed concentration peak. This illustrated the lack of equilibrium adsorption during the fast displacement of fluometuron through the soil. Also, the relative solution and adsorbed concentration distributions are flatter than those shown in Figures 8 and 9 for the slower average pore-water velocity. Spreading of the concentration distribution owing to nonequilibrium adsorption is inversely proportional to the adsorption or desorption kinetic rate coefficient for a given displacement rate[29]. Spreading is inversely proportional to the flow rate for constant rate coefficients[2].

The data in Figures 10 and 11 were not well described by the numerical solution of equation (13) with equilibrium adsorption. The data were consistently to the right of the calculated invading front. The kinetic adsorption and desorption models assisted in describing the nonequilibrium adsorption condition, but were not significantly better than the

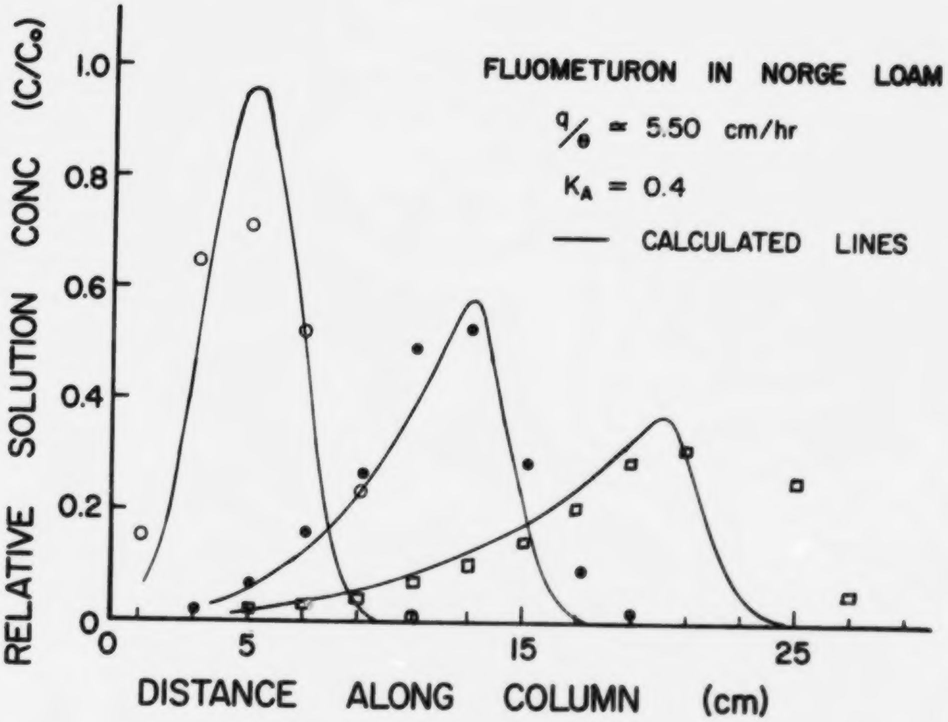

Figure 10. Calculated and experimental relative solution concentration distribution for 5.5 cm/hr average pore-water velocity. Calculated lines were obtained from a numerical solution of equation (14).

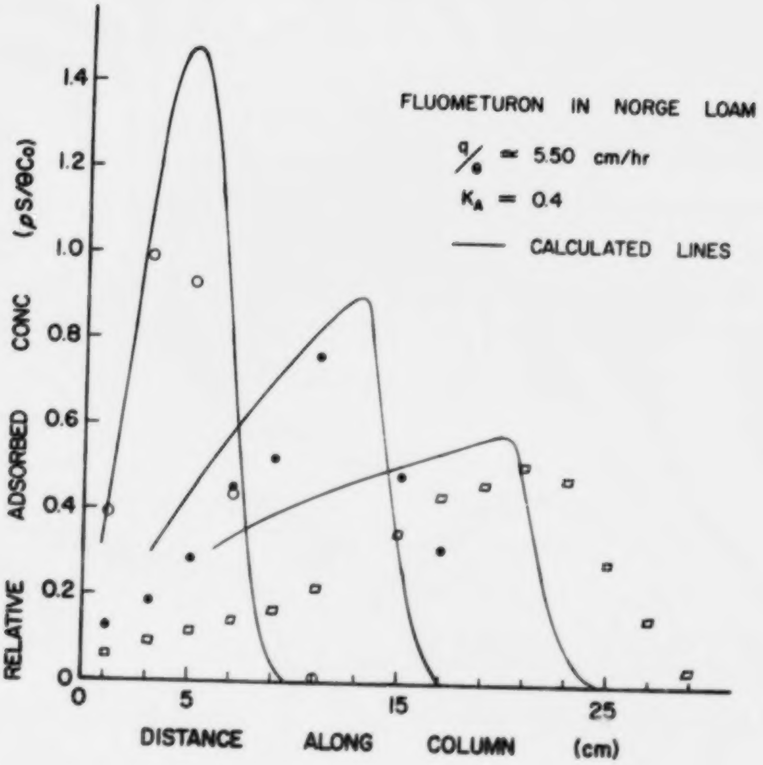

Figure 11. Calculated and experimental relative adsorbed concentration distribution for 5.5 cm/hr average pore-water velocity. Calculated lines were obtained from a numerical solution of equation (14).

equilibrium model[7 10]. The tailing produced by the non-singular characteristics of the adsorption-desorption process was described by the concentration dependent desorption distribution coefficient. One explanation for the right-hand shift of the data compared to the calculated line at the high flow rate is that the total surface area available to the herbicide during displacement may be less. If the mixing process was not complete during a herbicide's displacement, and estimate of the adsorption characteristics for the surface area contacted would be required. Similar results were obtained by van Genuchten et al.[10] for 4-amino-3,5,6-trichloropicolinic acid (picloram) effluent concentration distributions at high flow rates. They describe an empirical relationship for defining the fraction of the pore volume or soil surface area that was actively participating in adsorption and desorption at various flow rates. The procedure improved their ability to describe picloram concentration distributions in the effluent over a similar range in pore-water velocities to those used in this study.

The relative fluometuron concentration in the effluent from a water saturated column of Norge loam soil flowing at two different average pore water velocities is presented in Figure 12. These results illustrate the influence of flow rate on the adsorption-desorption process. The solid lines were calculated with an exact solution of equation (13)[4]. A kinetic adsorption model (equation [7]) was used and D was assumed to be negligible. The calculated lines are for the lower pore-water velocity. The distribution coefficient ($\theta k_A/\rho k_D$) for fluometuron and Norge loam was 0.31. The parameters associated with each calculated curve are the ratio between the kinetic desorption rate coefficient k_D and average pore-water velocity v_o. The kinetic desorption rate coefficient used for the three curves in Figure 12 from left to right were: k_D = 0.10, 0.55, and 5.5 hr^{-1}, respectively.

The shapes of the calculated curves in Figure 12 are a characteristic of k_D/v_o, and not the magnitude of the individual values comprising the ratio. For example, the same lines were calculated when the average pore-water velocity was 5.6 cm/hr and the k_D values were 1.0, 5.5 and

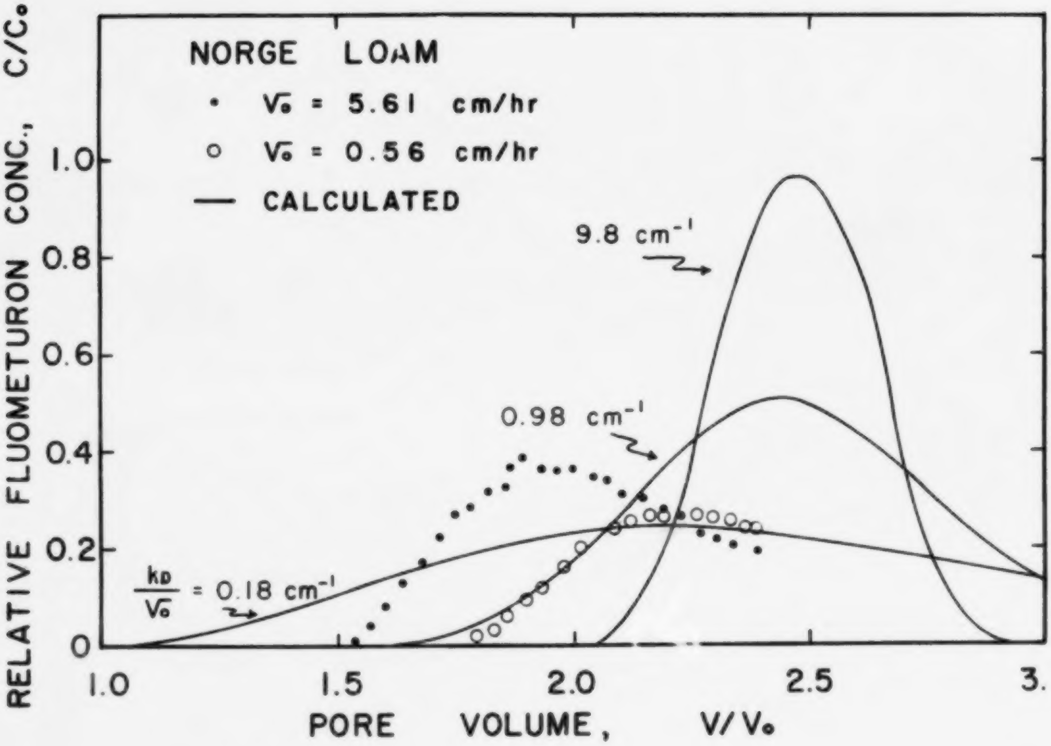

Figure 12. Calculated and experimental relative effluent concentration distribution from Norge loam soil. The calculated values were obtained using an exact solution of equation (13)[4] and various k_D/v_o values for the slow average pore-water velocity.

55 hr^{-1}, respectively. Note that the calculated effluent concentration distribution for a higher velocity (same k_D) than 0.56 cm/hr would be flatter and shifted to the left of that for a lower velocity. This is not the case for the measured effluent concentration distribution obtained from the high flow rate study, it has a higher maximum relative concentration as well as being shifted to the left. Figure 12 as well as the study by van Genuchten et al.[10] clearly illustrates the fact that the kinetic adsorption model does not adequately describe the mobility of a pesticide at high pore water velocities.

It should be pointed out that the kinetic desorption rate coefficient k_D, unless measured independently, could be selected on the basis of data fitting and thus erroneously include the spreading owing to dispersion. A major shortcoming of the analytical solution of equation (13)[4] is its inability to handle the nonsingular adsorption-desorption function and hydrodynamic dispersion.

In conclusion, the distributions of the adsorbed and solution phases of fluometuron were well described for a low flow rate using the numerical solution of equation (13) and the specific adsorption and desorption characteristics of the herbicide. The desorption distribution coefficient, K_D, was shown to be a function of the maximum amount of herbicide in solution prior to desorption. The movement of fluometuron at high flow rates was only approximated with kinetic adsorption and desorption parameters. At low flow rates where equilibrium adsorption exists, the kinetics of the adsorption process were not important. At high flow rates, the mobility of the herbicide is significantly influenced by a flow-rate dependent process. An empirical model presented by van Genuchten et al.[10] described the movement of picloram at high flow rates. The procedure defines a fraction of the adsorbing sites that was in equilibrium with the picloram during displacement. This fraction was a function of the average pore-water velocity. The procedure provided a reasonable fit between data and calculated effluent concentration distributions for a wide range of pore-water velocities. The dispersion coefficient must also be included in the model when evaluating solute transport at slow flow rates.

Transient Soil Water Study

The equilibrium adsorption and desorption isotherms for fluometuron and Cobb sand given in Figure 13 were described by the Freundlich equation (equation [10]). As can be seen in Figure 13, adsorption and desorption were not described by a single-valued function. For adsorption, the values of K_A and $1/N$ were 0.21 cm^3/g and 0.84, respectively. For desorption K_D and $1/N'$ were dependent upon the maximum amount of herbicide adsorbed. Table 3 gives the K_D and $1/N'$ values for each C_{max} studied. A reaction time of 30 min was sufficient for equilibrium adsorption; however, 8 hr was used to obtain all adsorption and desorption data.

Table 3. PARAMETERS ASSOCIATED WITH DESORPTION OF FLUOMETURON FROM COBB SAND AT 25 ± 0.5 C.

C_{max} µg/cm^3	K_D	$1/N'$
0.42	0.17	0.60
1.26	0.22	0.64
2.12	0.25	0.63
7.82	0.25	0.63
15.8	0.34	0.66
24.1	0.48	0.57
32.3	0.34	0.68
40.4	0.36	0.69

The N' in equation (11) was a function of C_{max}[10] (Table 3), but for this study was assumed constant. Using equation (12), the concentration dependent desorption distribution coefficient, K_D, was easily calculated

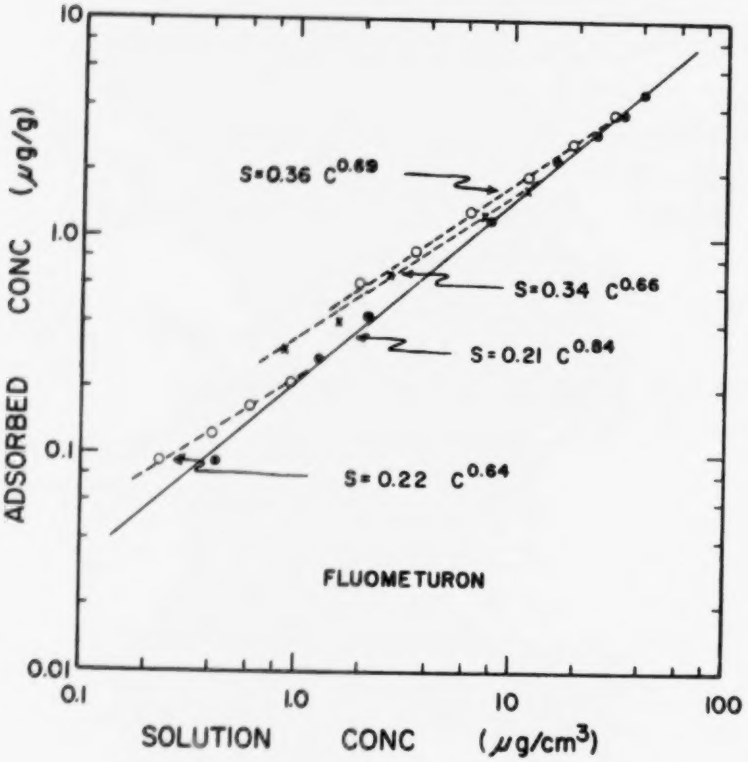

Figure 13. Adsorption and desorption isotherms for fluometuron on Cobb sand. Solid and broken lines are best fit for adsorption and desorption, respectively.

in the numerical solution. From preliminary desorption isotherm data at low herbicide concentrations, the average of the measured N' values was 1.7. This value was used to calculate the desorption distribution coefficient in the numerical solution. When all the desorption data over the concentration range given in Table 1 were collected the average N' was 1.5.

The fluometuron solution concentration with time at various soil depths during infiltration into Cobb sand is shown in Figure 14. The initial soil water content was 0.13 cm^3/cm^3 and the water flux at the soil surface was 1.03 cm/hr. These concentrations were determined by collecting samples of the soil-water through fritted filter discs during infiltration. The reduction in peak height and the increased spreading with depth shown in Figure 14 are a result of mixing by velocity dispersion and adsorption of the fluometuron in the soil. The tailing is an indication of the nonsingular relationship between adsorption and desorption.

Figures 15 and 16 show the adsorbed and solution fluometuron concentration distributions in Cobb sand. A one centimeter head of water was maintained on the soil surface throughout the infiltration process. These distributions were measured by taking samples from the soil columns immediately after the cessation of infiltration. The maximum adsorbed and solution concentrations generally occurred at approximately the same depth for all treatments. However, some lagging of the adsorbed phase is shown for the ponded infiltration into initially air-dry soil, Figure 15. This suggests that nonequilibrium adsorption conditions did not exist at the fast pore-water velocities associated with this column. The average filtration rate was 29.0 cm/hr for the initially dry soil and 10 cm/hr for the initially wet soil.

The initial soil-water content prior to infiltration had little effect on the displacement of fluometuron for a given quantity of infiltrated water. This is illustrated in Figure 17 where fluometuron concentrations are compared for initial soil-water contents of 0.005 (air-dry)

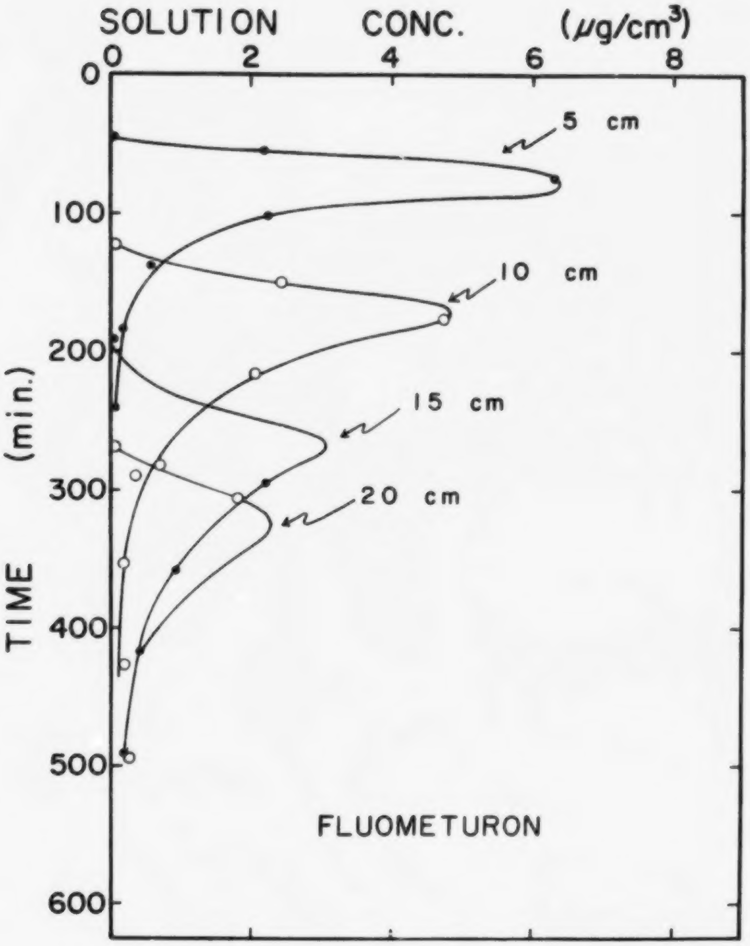

Figure 14. Fluometuron concentration distributions versus time for selected soil depths. The soil water flux and initial soil water content were 1.03 cm/hr and 0.13 cm^3/cm^3. Solid lines were eye fitted to experimental data.

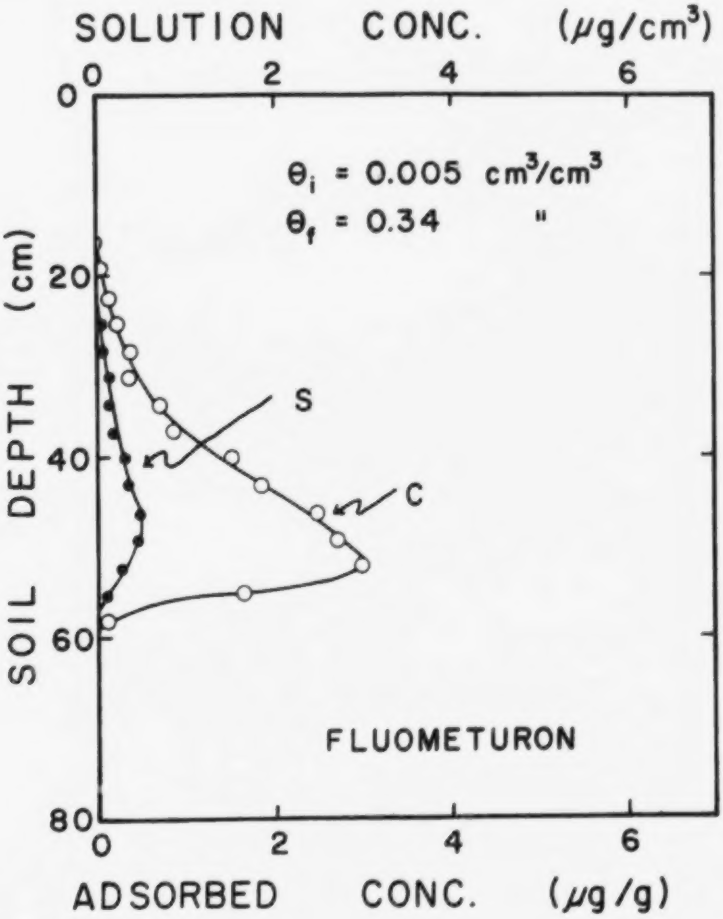

Figure 15. Solution and adsorbed fluometuron concentration distributions immediately following infiltration. Average soil-water flux was 29.0 cm/hr. The θ_i and θ_f are the initial and final volumetric soil water content in the soil surface region. Solid lines were eye fitted to experimental data.

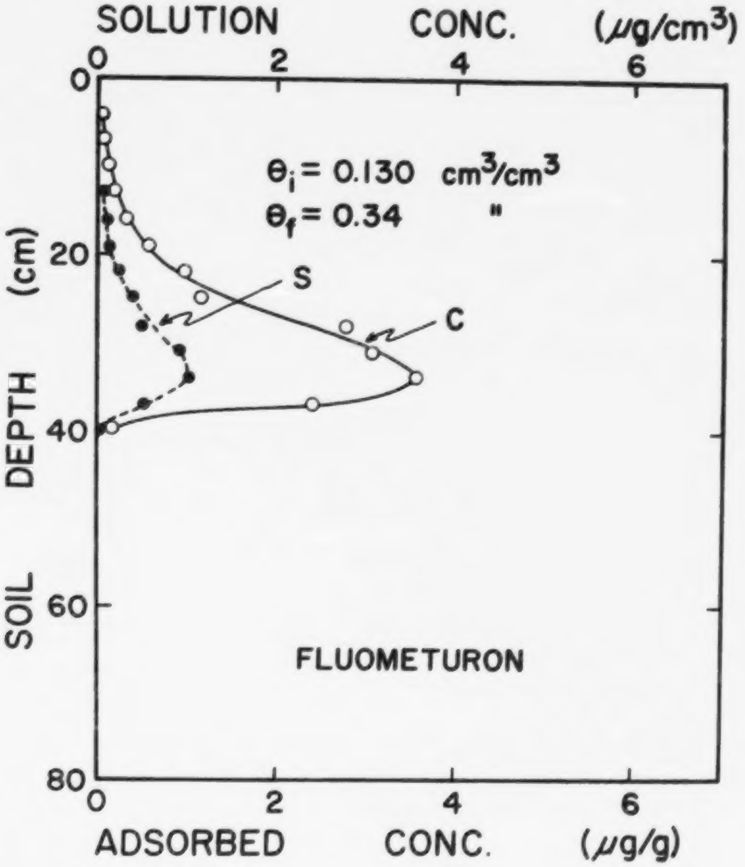

Figure 16. Solution and adsorbed fluometuron concentration distributions immediately following infiltration. Average soil-water flux was 10.0 cm/hr. The θ_i and θ_f are the initial and final volumetric soil water content in the soil surface region. Solid and dashed lines were eye fitted to experimental data.

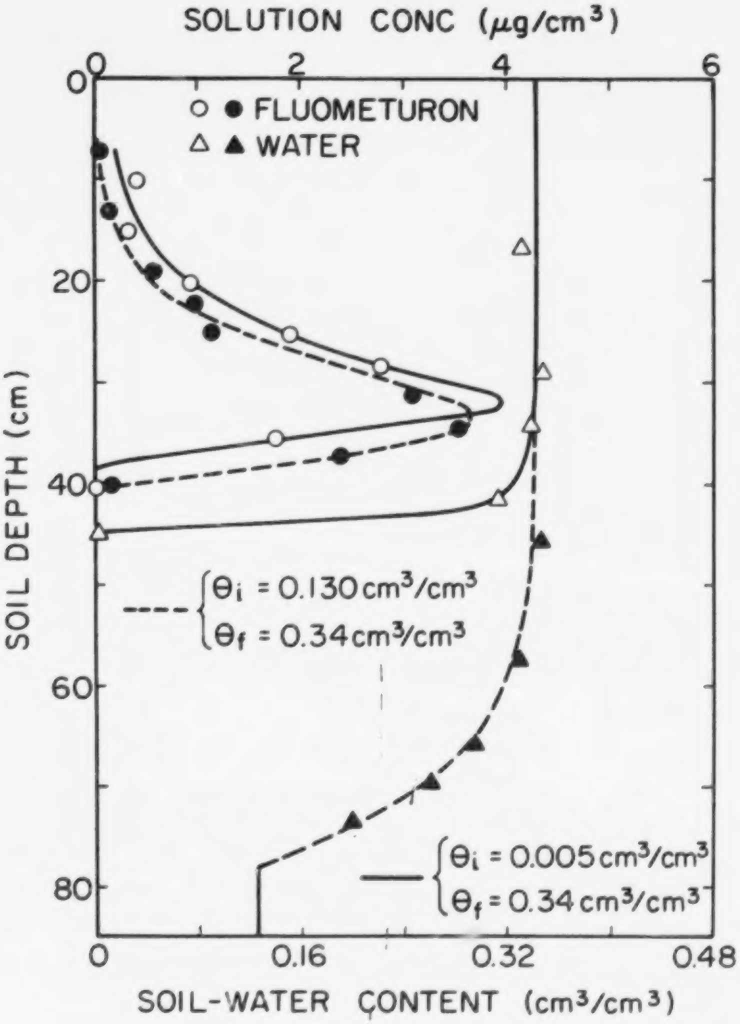

Figure 17. Fluometuron solution concentration and water content distributions for the same accumulative infiltration into an initially wet and dry soil. The θ_i and θ_f are the initial and final volumetric soil water content in the soil surface region. Solid and dashed lines were eye fitted to experimental data.

and 0.130 cm^3/cm^3. One centimeter of water was maintained on the soil surface of both columns throughout the infiltration process. The fluometuron displacement depths were relatively independent of the initial soil-water content, whereas the wetting front position was related to the initial soil water content. The fluometuron appears to move slightly deeper into the initially wet soil compared to the dry soil for the same amount of water. This was only true for experimental data and not the calculated distributions.

Figure 18 shows the influence of the water application rate and associated boundary conditions on the displacement of fluometuron. The cumulative infiltration was the same for both columns. The inverse relationship between leaching efficiency and surface water content shown here has been reported by several investigators (Keller and Alfaro[30], Warrick et al.[23], and Kirda et al.[14]). However, this inverse relationship was not necessarily valid when comparing fluometuron displacement for ponded and 5.0 cm/hr application rates. This was a result of the final soil-water content at the soil surface and in the transmission zone being only slightly different for these rates. Also, the smaller pore-water velocities during the 5.0 cm/hr application rate allowed more time for diffusion controlled adsorption to occur. The areas under the herbicide distribution curves in Figure 18 were not equal as a result of some fluometuron remaining at the soil surface for the 1.0 and 5.0 cm/hr application rates. At least a portion of this residual fluometuron appeared to be in solution. However, the validity of the measured fluometuron solution concentrations at the soil surface were questionable since some herbicide may have gone into solution as a result of the sampling procedure.

Experimental data from this study were used to determine the usefulness of a mathematical model for predicting herbicide displacement for transient flow conditions (Hybrid program, Appendix B). The model is similar to the one used by Kirda et al.[14]. The model used in this study includes an equilibrium adsorption or sink term (equation 13). The solute transport and water flow equations (equations [2] and [13]) were solved simul-

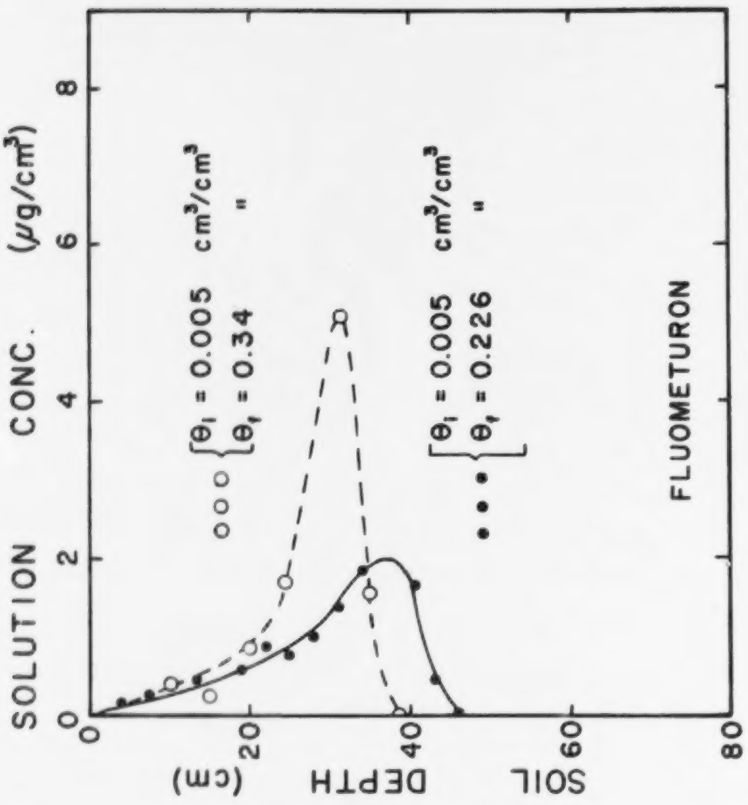

Figure 18. Fluometuron solution concentration distributions for equal accumulative infiltration into air-dry soil. The average soil water flux at the soil surface was 29.0 and 1.0 cm/hr. The θ_i and θ_f are the initial and final volumetric soil water content in the soil surface region. Solid and dashed lines were eye fitted to experimental data.

taneously in order to predict fluometuron and water distributions during infiltration. Equilibrium adsorption and desorption as described by equation (10) and (11) were also used. The dispersion coefficient, D, was assumed constant for each calculation, with a correction for numerical dispersion included.

Figures 19, 20, and 21 show comparisons of calculated and experimental distributions of fluometuron and water. The calculated fluometuron solution concentration distributions lagged behind the measured distributions in each case. However, the position of the peak concentration and the tailing edge seem to be predicted somewhat better for the slower, 4.89 cm/hr, infiltration rate (Figure 21) than for the soil columns on which water was ponded. These calculated distributions were obtained using values of 0.21, 0.84, and 0.59 for K_A, 1/N, and 1/N', respectively. The $D-\hat{D}_N$ value was dependent upon the water application rate and was 0.07 cm^2/hr for application rates of 1.0 and 5.0 cm/hr and 0.10 cm^2hr for columns on which water was ponded during infiltration. Equation (12) was used to calculate values of the distribution coefficient, K_D. The velocity and soil-water content terms used in the solute transport model were obtained from the numerical solution of the water flow equation (equation [2]).

As shown in Figures 19, 20, and 21, the numerical solution of equation (2) adequately described the measured soil-water content distributions. A uniform initial soil-water content distribution was used to approximate the soil-water content distribution for each initially wet soil column.

Van Genuchten et al.[10] have suggested that at high pore-water velocities equilibrium adsorption between all pore sizes may not exist, but that only a fraction of the soil participates in the adsorption process. If there was insufficient time for the fluometuron to diffuse into smaller pores at the high pore-water velocities existing in this study, then less adsorption than predicted would have occurred. To account for the non-adsorbing fraction, a term similar to the FREQ term used by van

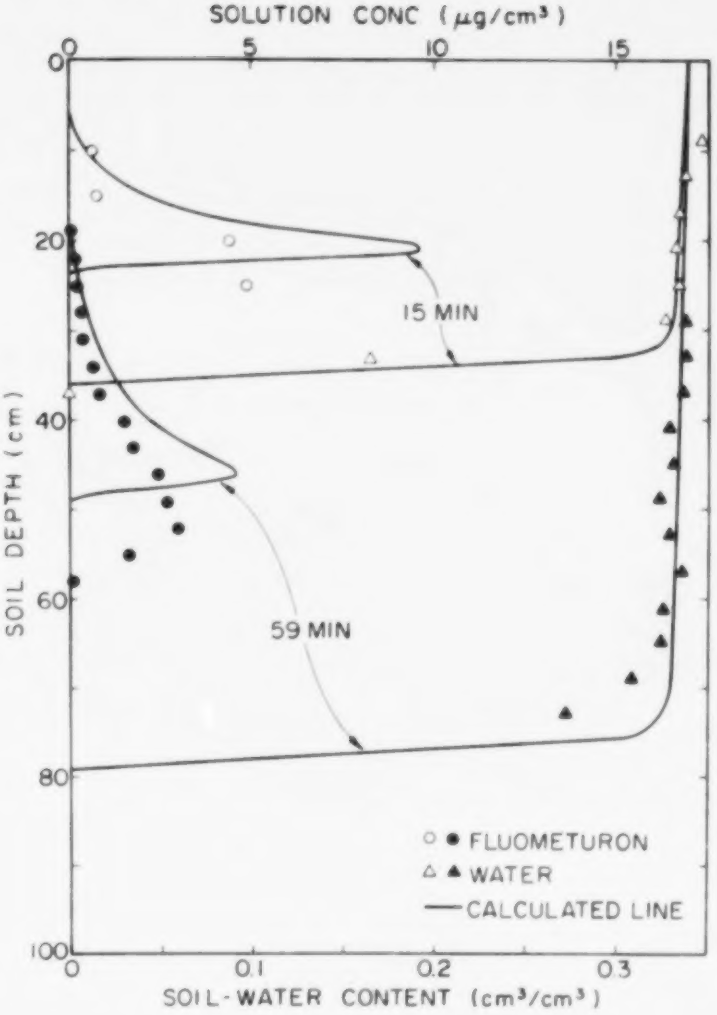

Figure 19. Experimental and calculated fluometuron solution concentration and water content distributions after 15 and 59 minutes of infiltration. Initial soil-water content was 0.005 cm^3/cm^3 and the average soil water flux was 29.0 cm/hr. Solid lines were calculated using equations (3) and (21).

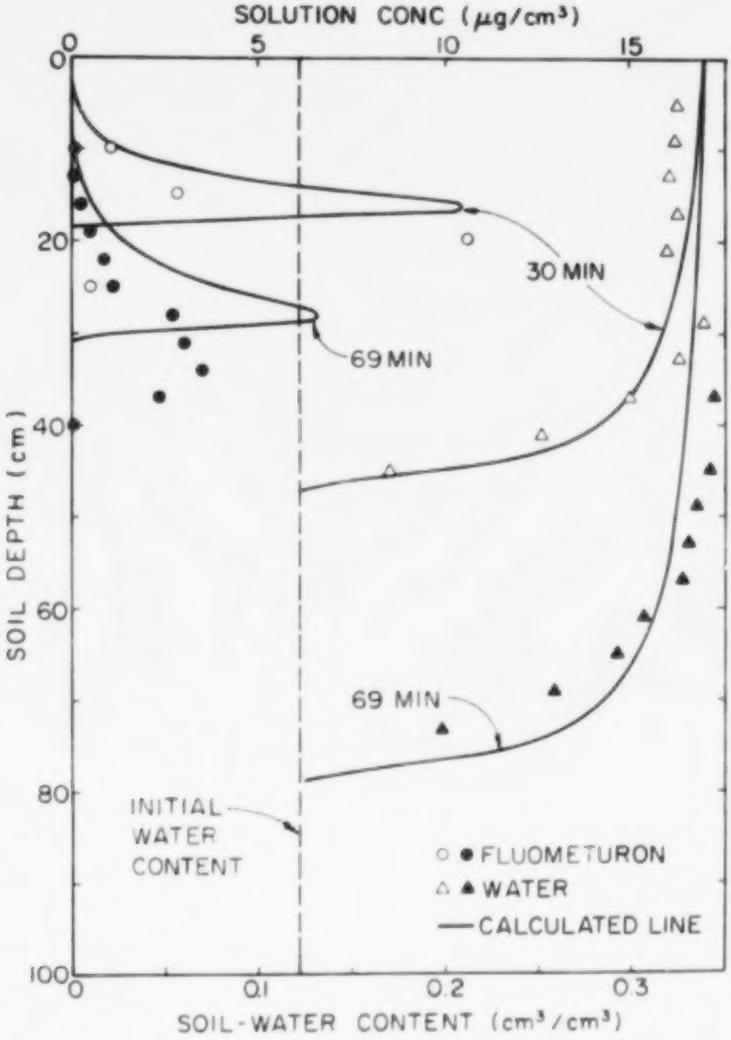

Figure 20. Experimental and calculated fluometuron solution concentration and water content distributions after 30 and 69 minutes of infiltration. Initial soil water content was 0.13 cm^3/cm^3 and the average soil-water flux was 10.1 cm/hr. Solid lines were calculated using equations (3) and (21).

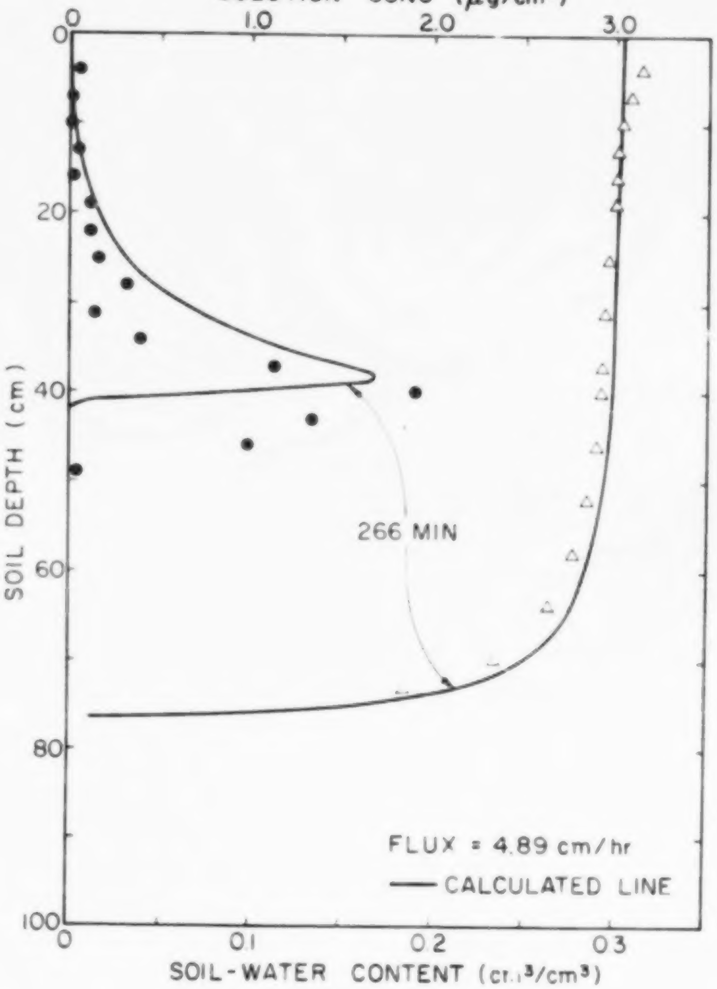

Figure 21. Experimental and calculated fluometuron solution concentration and water content distributions after 266 minutes of infiltration. Initial soil water content was 0.005 cm^3/cm^3 and the soil-water flux was 4.89 cm/hr. Solid lines were calculated using equations (3) and (21).

Genuchten et al.[10] was used in the calculations. The FREQ value was empirically determined and represented the fraction of soil participation in the adsorption process. Since the bulk density, ρ, is a measure of the mass of soil per unit volume, the FREQ term was multiplied by ρ to give a measure of the mass of soil per unit volume which was actively adsorbing and desorbing herbicide. The FREQ term was selected on the basis of its ability to describe the experimental data. It should be emphasized that a change in the ρ value as a result of multiplying it by FREQ does not indicate an actual change in the bulk density of the soil. Rather, it is an indication of a change in the surface area which was participating in the adsorption and desorption of fluometuron. For convenience and as a first approximation, the bulk density was used as a measure of the surface area of the soil. The model could be made more descriptive of the physical system by the addition of a surface area term.

Figure 22 gives the calculated fluometuron distributions for an initially wet soil on which water was ponded during infiltration. As can be seen, the tailing edge and the position of maximum concentration were described very well by using a FREQ value of 0.5, but the calculated peak concentration was much larger than the measured concentration. However, the calculated and measured maximum concentrations were approximately the same for other columns studied[31]. There also appears to be more dispersion at the displacing front than predicted by the model. The measured and calculated distributions of the adsorbed fluometuron for the conditions in Figure 22 are given in Figure 23. The solid line represents the distribution predicted for a ρ of 1.54 g/cm^3 and the broken line is the calculated line for a ρ of 0.77 g/cm^3 (FREQ = 0.5). As with the solution herbicide concentration, the model fails to describe the measured adsorbed herbicide concentration distributions when all the soil was assumed to be in equilibrium with the herbicide. When it was assumed that only half of the soil material is actively participating in the adsorption process (ρ = 0.77 g/cm^3), the calculated and experimental curves agree very well.

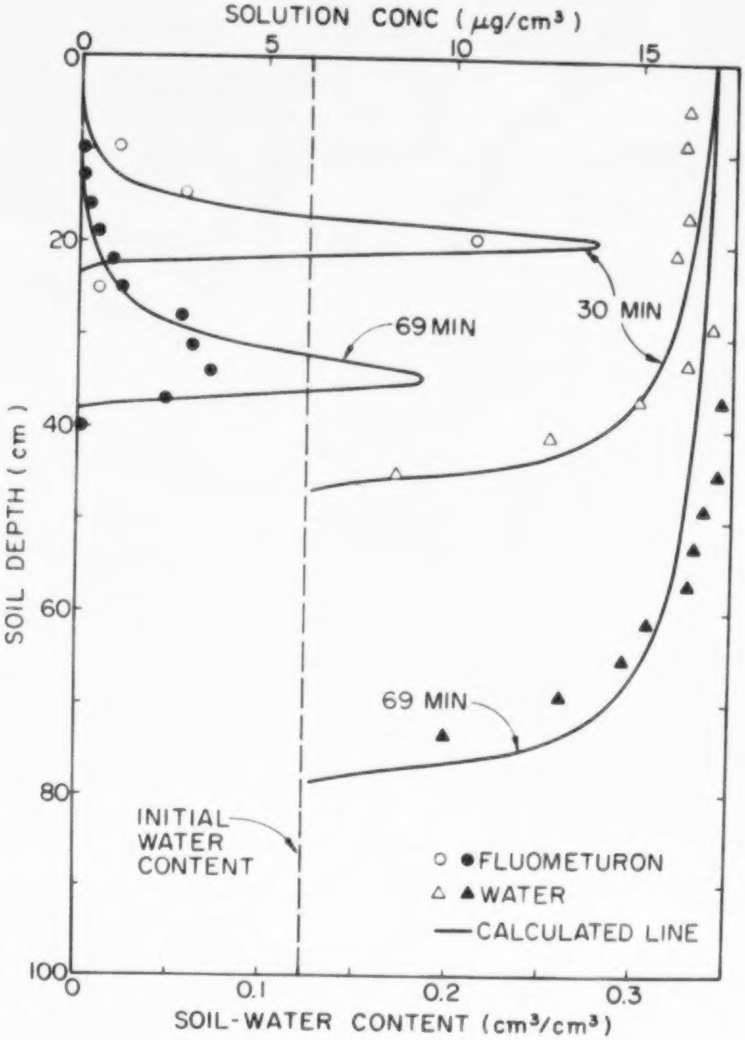

Figure 22. Experimental and calculated fluometuron solution concentration and water content distributions after 30 and 69 minutes of infiltration. Initial soil water content was 0.13 cm^3/cm^3 and the average soil-water flux was 10.1 cm/hr. Solid lines were calculated using equations (3) and (21) for ρ = 0.77 g/cm^3 (FREQ = 0.5).

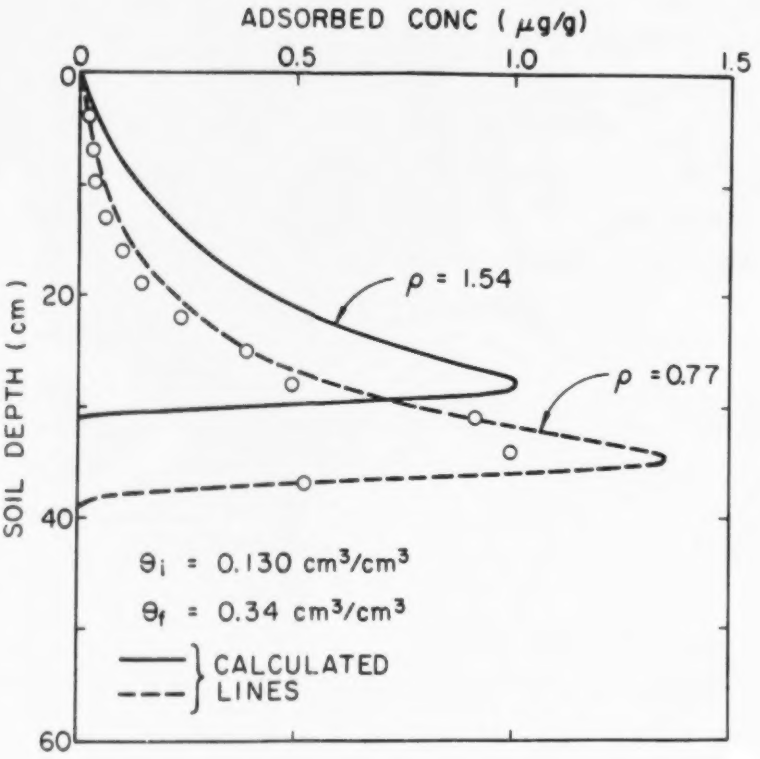

Figure 23. Experimental and calculated adsorbed fluometuron concentration distribution. The θ_i and θ_f are the initial and final volumetric soil water content in the soil surface region. The average soil-water flux was 10.1 cm/hr. Solid and dashed lines were calculated for $\rho = 1.54$ and 0.77 g/cm^3 (FREQ = 0.5).

The failure of the model to describe the shape of the displacing fluometuron front results from using a constant value for the dispersion coefficient and/or too low a value (equation [23]). The velocity dependence of the dispersion coefficient has been shown by several investigators[9 14 25].

In general, the mathematical model adequately described the shape and position of the fluometuron and water distributions when a FREQ term was used to account for the fraction of the total surface area participating in the adsorption process. However, further studies need to be conducted on the influence of pore-size distribution and pore-water velocity on the adsorption and dispersion of pesticides moving through soil. Also, the usefulness of the mathematical model used in this study (Appendix B) should be evaluated with additional laboratory and field data. Of particular interest would be the ability of this model to describe herbicide movement for infiltration rates and associated pore-water velocities small enough to allow greater radial diffusion of the herbicide.

FIELD EXPERIMENTS

The data for each rainfall intensity study are presented as two individual "replications". Due to differences in water amounts required to obtain runoff, slight differences in catchment and border installation, initial fluometuron concentrations, and a one-day interim between water application to the two replicate plots, it was felt each plot was an individual entity.

Rainfall intensity had no measurable effect on fluometuron concentrations or total herbicide losses in the runoff (Table 4). There was a trend toward lower runoff concentrations and total herbicide losses at the intermediate rainfall intensity. However, the fluometuron loss from all plots was very low. The first 3.78 L of runoff water contained a higher concentration than did the composite of the next 41.6 L. Apparently, the fluometuron concentration in solution was decreasing with increased volumes of water runoff. The sediment concentrations of fluometuron were much higher than the concentrations in water. The fluomet-

Table 4. THE EFFECT OF RAINFALL INTENSITY ON THE CONCENTRATION AND PERCENT OF APPLIED FLUOMETURON IN RUNOFF WATER AND SEDIMENT

Rainfall frequency	Initial concentration[a]	Water				Sediment		Total % loss
		3.78 L[b]		3.78-45.4 L[c]				
		µg/ml	%	µg/ml	%	µg/g	%	
Fast	5.7 ± 0.42	0.12 ± 0.008	0.02	0.12 ± 0.008	0.16	4.1 ± 0.25	0.02	0.20
Fast	4.1 ± 0.25	0.10 ± 0.006	0.02	0.06 ± 0.003	0.12	2.8 ± 0.13	0.01	0.15
Intermediate	5.7 ± 0.42	0.08 ± 0.004	0.01	0.03 ± 0.001	0.04	2.9 ± 0.14	0.01	0.06
Intermediate	4.1 ± 0.25	0.09 ± 0.005	0.01	0.05 ± 0.002	0.09	2.3 ± 0.009	0.01	0.11

[a] The concentration of fluometuron (µg/g) chemically determined to be in the top 5 cm of soil sampled immediately after herbicide application.

[b] The concentration and percent loss of fluometuron in the first 3.78 L of runoff water from the plot.

[c] The concentration and percent loss of fluometuron in the next 41.6 L composite of runoff water.

uron concentration ratio between the water and sediment was higher than would be expected based upon adsorption data for the soil[7]. It has been shown by Hornsby and Davidson[7] that adsorption and desorption of fluometuron were not single valued. Once the soil particles were suspended in the runoff, the fluometuron evidently does not desorb back along the adsorption isotherm. The relationship between the herbicide and sediment, during runoff, appears to be more closely related to the desorption than the adsorption isotherm. Although the concentration of fluometuron was lowest in the 41.6 L composite fraction, the total loss was greater due to the larger amount of water. Though sediment fluometuron concentrations were high, very little herbicide was actually lost in this phase since sediment losses were very low. The magnitude of fluometuron losses were being influenced by the volume of water and the amount of sediment leaving the target site.

Chemical and bioassay analysis data for vertical fluometuron movement (Table 5) showed a deeper movement trend with continuous rainfall; however, this trend was not well defined. Water was applied to the plots until the desired runoff was obtained, and this amount varied among plots. The deeper movement in one replication at the fast intensity could be due to more water being applied to the plot or experimental error. Deeper fluometuron movement into a soil column at high compared to low water flow rates has been reported by Hornsby and Davidson[7] for laboratory studies. Also, at the fast water application rate it may have been possible to exceed equilibrium adsorption due to a high infiltration rate; thus, producing a deeper movement of the herbicide into the soil. At the slow rainfall intensity, rainfall was applied over a 4-day period and some water was lost by evaporation during this period. As a result, less water actually entered the soil and was available for movement through the profile. For all treatments, fluometuron moved into the 5-10 cm soil depth. In general, the bioassay analysis indicated a lower concentration of fluometuron present than did the chemical analysis method. This was not surprising in that the chemical analysis method detects fluometuron and all its metabolites down to 3-trifluoro-methyl aniline. Thus, less toxic breakdown products would

Table 5. CHEMICAL AND BIOASSAY ANALYSIS OF FLUOMETURON AT THREE SOIL DEPTHS FOR DIFFERENT RAINFALL INTENSITIES

Rainfall frequency	Rainfall amount, cm	Initial conc.[a] 0-5 cm Chem.	Initial conc.[a] 0-5 cm Bio.	Post-rainfall conc., µg/g 0-5 cm Chem.	Post-rainfall conc., µg/g 0-5 cm Bio.	Post-rainfall conc., µg/g 5-10 cm Chem.	Post-rainfall conc., µg/g 5-10 cm Bio.	Post-rainfall conc., µg/g 10-20 cm Chem.	Post-rainfall conc., µg/g 10-20 cm Bio.
Fast	7.5	5.7 ± 0.42	4.0	3.0 ± 0.19	2.2	1.5 ± 0.04	1.9	0.8 ± 0.01	0.5
Fast	6.3	4.1 ± 0.25	2.5	1.7 ± 0.05	1.5	1.2 ± 0.02	1.4	0 < ± 0.01	0
Intermediate	6.3	5.7 ± 0.42	4.0	2.8 ± 0.13	2.3	0.6<± 0.01	1.0	0 < ± 0.01	0
Intermediate	5.6	4.1 ± 0.25	2.9	2.1 ± 0.08	1.0	0.9 ± 0.01	1.1	0 < ± 0.01	0
Slow	6.3	3.5 ± 0.19	3.2	2.3 0.09	1.3	0.4<± 0.01	2.5	0 < ± 0.01	0
Slow	6.3	4.5 ± 0.29	4.1	2.8 ± 0.13	2.4	1.1 ± 0.02	1.4	0 < ± 0.01	0

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[a] Fluometuron concentration (µg/g) in the top 5 cm of soil immediately after application. Chem. means chemical assay, and bio. means bioassay results.

be detected chemically but not by bioassay. It is also possible that the herbicide in the laboratory prepared soil standards may be more available than that in the field samples subjected to environmental variations. In addition, the bioassay species was not sensitive to small differences at the higher fluometuron concentrations since at these concentrations (above 2 μg/g) the plant was killed.

Using the "Hybrid" program for transient soil water conditions (Appendix B), the total fluometuron concentration distribution in Teller sandy loam following infiltration (5.7 cm of water) and two days of evaporation (-0.02 cm/hr) and redistribution was calculated. Figure 24 shows the agreement between the calculated and experimental fluometuron distributions. The soil water content distribution prior to infiltration, at the cessation of infiltration and 48 hours after infiltration are also shown in Figure 24. The adsorption distribution coefficient, N and N' were: 0.66, 1.19 and 1.70, respectively. The agreement between the calculated and experimental fluometuron concentration distributions was reasonable and would be satisfactory for simulation of most field problems. These calculations also illustrate the versatility of the "Hybrid" program for describing the movement and distribution of water and pesticides in soils.

Antecedent soil moisture significantly influenced fluometuron concentrations in the water and on the sediment as well as the total losses by runoff (Table 6). A lower initial concentration of fluometuron was applied to these plots compared to the rainfall intensity experiment. Consistent with the results of the fast rainfall intensity experiment, runoff from the antecedent dry plots contained very low herbicide concentrations in the water, but higher concentrations on the sediment. However, when the fluometuron was applied to the wet soil and rainfall simulated, runoff losses were much higher. The concentrations in the first 3.78 L of water was above 0.6 μg/ml, but the concentration decreased substantially in the next 41.6 L. The herbicide concentrations on the sediment were approximately twice those from the dry plots. The

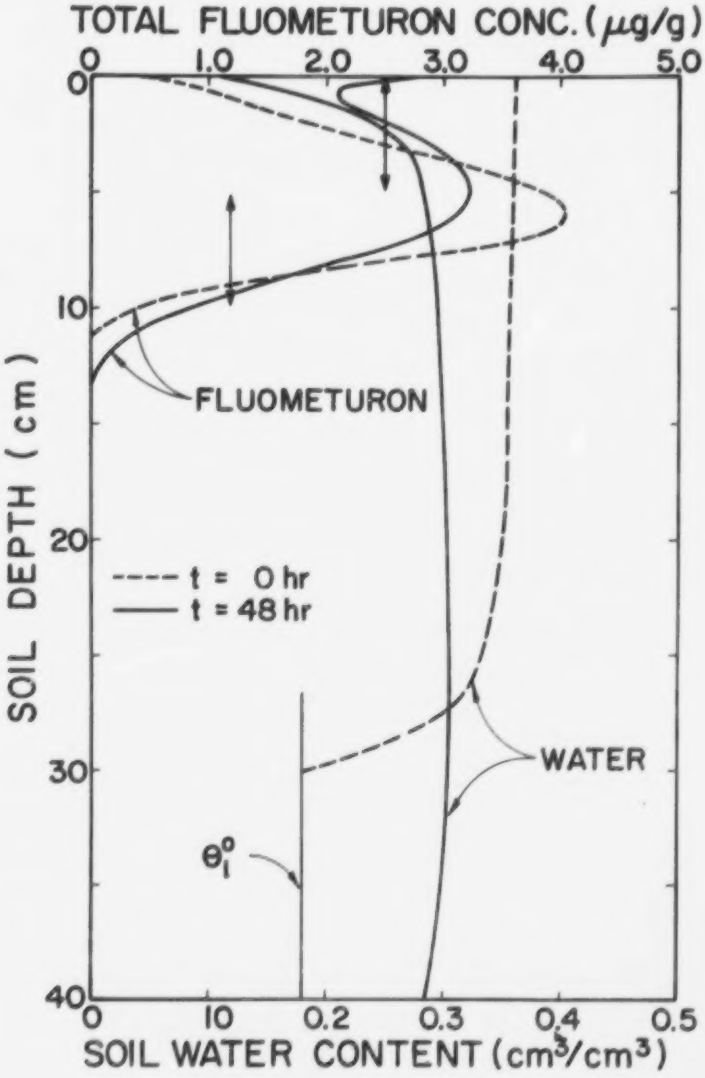

Figure 24. Experimental and calculated total (solution and adsorbed) fluometuron concentration distribution in Teller sandy loam soil following infiltration of 5.7 cm of water (t=0) and 48 hours of evaporation (-0.02 cm/hr) at the soil surface. The initial soil water content was 0.18 cm^3/cm^3. The vertical lines are the average measured fluometuron concentration in these regions under natural field conditions following 5.7 cm of water infiltration and 48 hours of evaporation and redistribution.

Table 6. THE EFFECT OF ANTECEDENT SOIL WATER CONTENT ON THE CONCENTRATION AND PERCENT OF THE APPLIED FLUOMETURON IN THE RUNOFF WATER AND SEDIMENT

Antecedent soil moisture	Initial conc.[a]	Water				Sediment		Total % loss
		3.78 L[b]		3.78-45.4 L[c]				
		μg/ml	%	μg/ml	%	μg/g	%	
Dry	2.4 ± 0.10	0.06 ± 0.003	0.01	0.03 ± 0.001	0.07	1.8 ± 0.06	0.02	0.10
Wet	2.2 ± 0.08	0.63 ± 0.05	0.21	0.21 ± 0.015	0.74	3.1 ± 0.16	0.02	0.96

[a] The concentration of fluometuron (μg/g) chemically determined to be in the top 5 cm of soil sampled immediately after herbicide application.

[b] The concentration and percent loss of fluometuron in the first 3.78 L of runoff water from the plot.

[c] The concentration and percent loss of fluometuron in the next 41.6 L composite of runoff water.

losses from the individual wet plots were 0.83 and 1.09% of that applied. These plots were wetter than would normally be the case when using surface application techniques, but might be characteristic of conditions during an aerial application.

The wet plots required approximately one-half the volume of simulated rainfall to produce runoff compared to the dry plots. As a result, less fluometuron was leached into the profile (Table 7). Less movement into the profile would leave a higher concentration of herbicide on the surface and available for removal from the target site. The chemical and bioassay analyses were in close agreement. No herbicide was shown to move deeper than the 5-10 cm depth in the wet plots.

Table 7. CHEMICAL AND BIOASSAY ANALYSIS OF FLUOMETURON AT THREE SOIL DEPTHS FOR DIFFERENT RAINFALL INTENSITIES

Antecedent soil moisture	Rainfall amount, cm	Initial conc.[a]		Soil depth			
				0-5 cm		5-10 cm	
		Chem.	Bio.	Chem.	Bio.	Chem.	Bio.
Dry	5.3	2.4 ± 0.10	2.3	2.0 ± 0.07	2.1[b]	0.3 <± 0.01	<0.5
Wet	2.8	2.2 ± 0.08	2.3	2.2 ± 0.08	1.8	0.0 <± 0.01	0.0

[a] Fluometuron concentration (μg/g) in the top 5 cm of the profile immediately after application.

[b] Fluometuron concentrations expresses as μg/g of soil.

Plots from the rainfall intensity experiment were sampled at three dates to determine fluometuron movement and dissipation (Table 8 and 9). Bioassay analyses were not conducted on samples from the 20-30 cm depth. In general, the bioassays again indicated lower concentrations but both

Table 8. CHEMICAL ANALYSIS OF FLUOMETURON IN THE SOIL PROFILE OVER AN EIGHTY-FOUR DAY PERIOD

Initial conc.[a]	Rainfall frequency & amount, cm[b]	Soil depths, cm sampled 7/2/73			Soil depths, cm sampled 7/26/73				Soil depths, cm sampled 9/24/73			
		0-5	5-10	10-20	0-5	5-10	10-20	20-30	0-5	5-10	10-20	20-30
5.7	Fast-7.5	3.0[c]	1.5	0.8	3.0	1.5	0.8	0.3	2.6	1.9	1.3	0.3
4.1	Fast-6.3	1.7	1.2	0	1.5	0.9	0	0	1.6	1.1	0.2	0
5.7	Int.-6.3	2.8	0.6	0	2.8	1.0	0	0	2.3	0.8	0.1	0
4.1	Int.-5.6	2.1	0.9	0	2.3	0.6	0	0	1.4	0.8	0.1	0
3.5	Slow-6.3	2.3	0.4	0	2.3	0.8	0	0	1.7	0.9	0.2	0
4.5	Slow-6.3	2.8	1.1	0	2.1	0.6	0	0	1.4	1.1	0.2	0

[a] Fluometuron concentration (μg/g) in the top 5 cm of the profile immediately after application.

[b] Applied immediately after herbicide application by simulated rainfall.

[c] Fluometuron concentration in μg/g of soil.

Table 9. BIOASSAY ANALYSIS OF FLUOMETURON IN THE SOIL PROFILE OVER AN EIGHTY-FOUR DAY PERIOD

Initial conc.[a]	Rainfall frequency & amount, cm[b]	Soil depths, cm sampled 7/2/73			Soil depths, cm sampled 7/26/73			Soil depths, cm sampled 9/24/73		
		0-5	5-10	10-20	0-5	5-10	10-20	0-5	5-10	10-20
4.0	Fast-7.5	2.2[c]	1.9	0.5	1.1	0.7	0.5	0.9	0.7	0.6
2.5	Fast-6.3	1.5	1.4	0	0.8	0.5	0	0.8	0.5	0
4.0	Int.-6.3	2.3	1.0	0	2.8	1.0	0	1.6	1.1	0
2.9	Int.-5.6	1.0	1.1	0	1.6	0.9	0	1.0	1.0	0.5
3.2	Slow-6.3	1.3	<0.5	0	1.3	0.4	0	0.6	0.7	0
4.1	Slow-6.3	2.4	1.4	0	2.6	1.6	0	1.6	0.9	0.4

[a] Fluometuron concentration (μg/g) in the top 5 cm of the profile immediately after application.

[b] Applied immediately after herbicide application by simulated rainfall.

[c] Fluometuron concentration in μg/g of soil.

methods indicated similar trends. On the final sampling date, fluometuron was shown to be in the 10-20 cm soil layer on all plots and the 20-30 cm layer on one plot by chemical analysis, but bioassay did not indicate the presence of fluometuron at all depths. However, most concentrations in the 10-20 cm zone were below the limit of bioassay detection. Although attenuation was occurring, fluometuron remained at phytotoxic concentrations to oats 84 days after application. In general, the rainfalls between July 26, 1973 and September 24, 1973 were small and did not produce significant runoff. Also, because of evaporation the downward penetration of the water was not sufficient to move the fluometuron deeper into the soil profile.

The water bioassay procedure for fluometuron, described by Truelove[27], was found to accurately predict herbicide concentrations. Since the results of selected samples analyzed by bioassay and chemical methods were in close agreement, only the chemical assay results were presented.

The distribution of a pesticide within a soil profile with time was simulated for steady state soil water flow (Appendix A) and is shown in Figure 25. The chemical was initially distributed uniformly in the top 15 cm of the soil profile at a rate of 2.24 kg/ha. The adsorption distribution coefficient, N and N' were: 0.21, 1.19 and 1.7, respectively. The soil water was assumed to be moving under unit gradient below the plant root zone at a soil water flux of 0.128 cm/day. The soil water content was 0.20 cm^3/cm^3 and represents the field water content in Cobb sand (soil used in transient laboratory experiment) in the region below the plant root zone. Biological degradation of the pesticide was assumed to be absent. The maximum pesticide concentration decreased with time and the distribution becomes more skewed as the chemical moved deeper into the profile. Once the chemical was below the plant root zone (150-180 cm or 5-6 feet), the situation described in Figure 25 would be similar to a natural occurring field condition in an irrigated region. Using this procedure and a biological degradation submodel, the fate of a pesticide could be simulated prior to using it in an agricultural program.

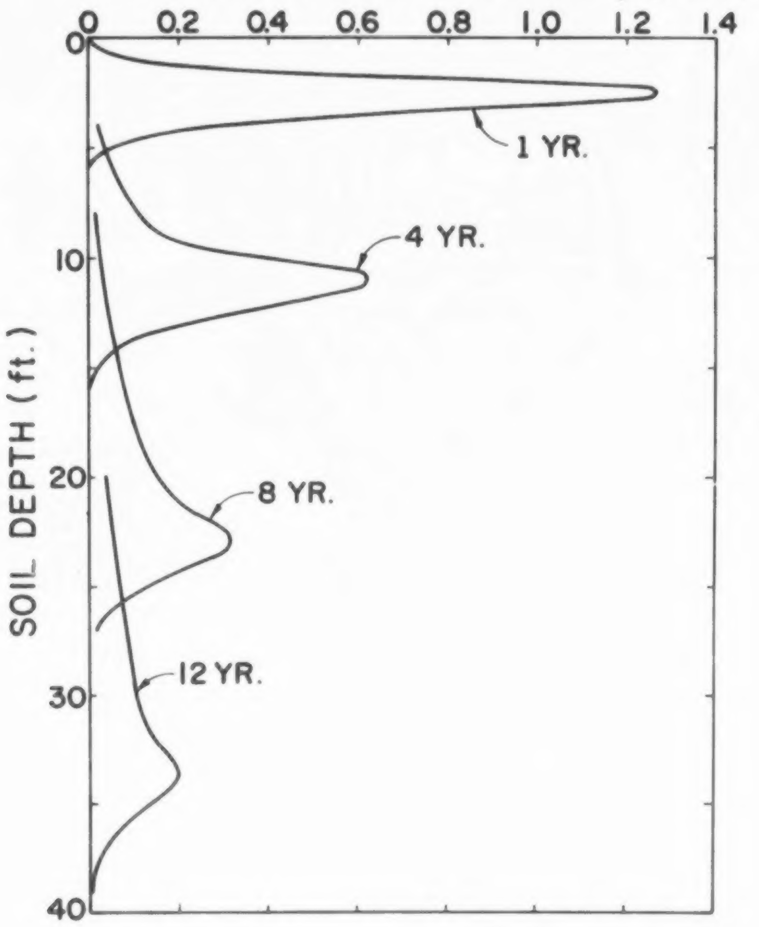

Figure 25. Simulated pesticide distribution in a soil profile with time for steady state soil water conditions. Average soil water content, water flux, distribution coefficient, N and N' were 0.20 cm^3/cm^3, 0.128 cm/day, 0.21, 1.19, and 1.7, respectively.

SECTION VII

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SECTION VIII

GLOSSARY

A = quantity of pesticide applied to the soil surface or introduced at $z = 0$ ($\mu g/cm^2$)

C = pesticide solution concentration ($\mu g/cm^3$)

C_m = maximum pesticide solution concentration prior to desorption ($\mu g/cm^3$)

D = apparent diffusion or dispersion coefficient (cm^2/hr)

D_n = correction for numerical dispersion in finite difference solution of one solute transport equation (cm^2/hr)

$\hat{D}_N$ = correction for numerical dispersion in finite difference solution of solute transport equation with G and K_A equal to zero (cm^2/hr)

G = correction for numerical dispersion in finite difference solution of solute transport equation for transient soil water conditions

ΔG_A^{+}, ΔG_P^{+} = free energy of activation for adsorption and desorption

I = infiltration rate (cm/hr)

I = infiltration rate (cm/hr)

K = hydraulic conductivity (cm/hr)

K_m = maximum hydraulic conductivity at cessation of infiltration (cm/hr)

K_{max}^{j-1} = maximum hydraulic conductivity in soil profile at j-1 time after the initiation of evaporation and/or redistribution of water (cm/hr)

K_A, K_D = adsorption and desorption partition or distribution coefficient

N = constant that varied with pesticide and adsorbent

$Q = \partial\theta/\partial h$

R = gas constant

S = adsorbed pesticide concentration (μg/g)

S_{max} = maximum adsorbed pesticide concentration prior to desorption (μg/g)

T = absolute temperature

$$X_i^j = \frac{q}{\theta}{}_i^j - \frac{D}{\theta}{}_i^j \; \frac{\theta_{i+1}^j - \theta_{i-1}^j}{2\Delta z}$$

h = soil water pressure (cm)

i = space or depth indice

j = time indice

k_A, k_D = adsorption and desorption rate coefficients (hr^{-1})

k'_A, k'_D = constant generally referred to as frequency factor of adsorption and desorption (hr^{-1})

q = volumetric soil-water flux (cm/hr)

t = time (hr)

z = soil depth measured positive downward (cm)

θ = volumetric water fraction (cm^3/cm^3)

ρ = bulk density (g/cm^3)

τ = variable of integration

ϕ = hydraulic head (cm)

APPENDIX A

Computer Program for Solute Transport Under Steady State Soil Water Conditions

INPUT-OUTPUT

DATA FORMAT

The following details the input data. Each DATA SET represents a READ statement in the program. Some data sets are required, others are dependent upon other input variables read in. Do these in order unless otherwise directed.

DATA SET 1: FORMAT (5I5) Required only once

Read NTOTAL

NTOTAL = Total number of runs to be made, each run describing its own system.

DATA SET 2: FORMAT (5I5) Required NTOTAL times

Read N, NUMBER, IXXX, INTERT, NOVRID

N = For N=0, output printouts will be C vs. X. For N=1, output printouts will be C vs. time (and pore volume).

NUMBER = Use only for N=0; the number of different time values for which C vs. X will be printed.

IXXX = Merely an identification number distinguishing the run.

INTERT= For INTERT=1, program will generate chemical at soil surface for a time T. For INTERT=0, the chemical is initially distributed within the soil.

NOVRID= For NOVRID=1, read in on a card an initial C/CO distribution. For NOVRID=0, the program puts a square pulse distribution in initially.

DATA SET 3: FORMAT (5F15.5) Required NTOTAL times

Read VEL, D, K, THETA, RHO, CO, XMAX, T, NEXP, AB, PULSE, KTIME, H

VEL= A constant velocity.

D= Dispersion coefficient. Includes correction for numerical dispersion associated with finite difference calculations.

K= The absorption coefficient, $S=KC^N$.

THETA= The water content θ.

RHO= The bulk density of the soil.

CO= The magnitude of input chemical concentration.

XMAX= The length, or depth in the soil which is farther than the chemical will ever reach.

T= For INTERT=1, specify the time for which chemical will enter at the soil surface. If INTERT=0, T need not be specified.

NEXP= The exponent N on $S=KC^N$.

AB= The exponent AB on $S=K_dC^{1/AB}$

PULSE= For INTERT=0, specify the distance as measured from x=0 for which there will be a non-zero initial C distribution. For INTERT=1, PULSE need not be specified.

KTIME= The constant time increment Δt, used to calculate C(J). Not to be confused with DELT.

H= The x increment used in the calculations.

DATA SET 4: FORMAT (5F15.5) Optional NTOTAL times

If INTERT=0 and NOVRID=1, read data set 4, or else go to data set 5.

Read CNST

CNST= The constant initial concentration C/CO which is initially distributed from x=0 to x=PULSE.

(NOTE: Data set 4 can easily be modified to accept as input any initial distribution of C/CO for each x point from x=0 to x=PULSE by making a few changes in the program. At the time of this writing, we had not done so in the Chemical Program.)

DATA SET 5: FORMAT (5F15.5) Optional NTOTAL times

If N=0, go to data set 6; if N=1, read data set 5.

Read DELT, TMAX, X, STARTT

DELT= For printouts, a value of C/CO will be printed every DELT units of time.

TMAX= For printouts, the program will halt this particular run when time=TMAX.

X= For printouts, the C/CO value will always be printed out for the point which is a value of X down the soil profile.

STARTT= For printouts, values of C/CO will be printed starting at time=STARTT, continuing until time= TMAX, printed every DELT.

(NOTE: If data set 5 was used, the next data set to be read in is data set 2, if NTOTAL>1).

DATA SET 6: FORMAT (2F15.5) Optional NTOTAL times

If N=0, read data set 6, or else go to data set 5.

Read DELX, TIMER

DELX= For printouts, at time-TIMER, C/CO values will be printed starting at x=0 and every DELX thereafter until XMAX.

TIMER= C/CO will be printed out vs X whenever time-TIMER.

(NOTE: Data set 6 has to be executed a grand total of NUMBER times. After NUMBER cards have been read in, each with a DELX, TIMER pair on it, then the next data set to be read in is data set 2, if NTOTAL 1).

END OF DATA SETS

An example of input data to the chemical equation is below.

```
data set 1      2.

data set 2      0.          3.       1021.        1.         0.

data set 3      5.           .02         .4        .366      1.54
               90.         30.          2.3        .88       2.5
                0.           .01         .2

data set 6       .2         2.
                 .2         4.
                 .4         6.

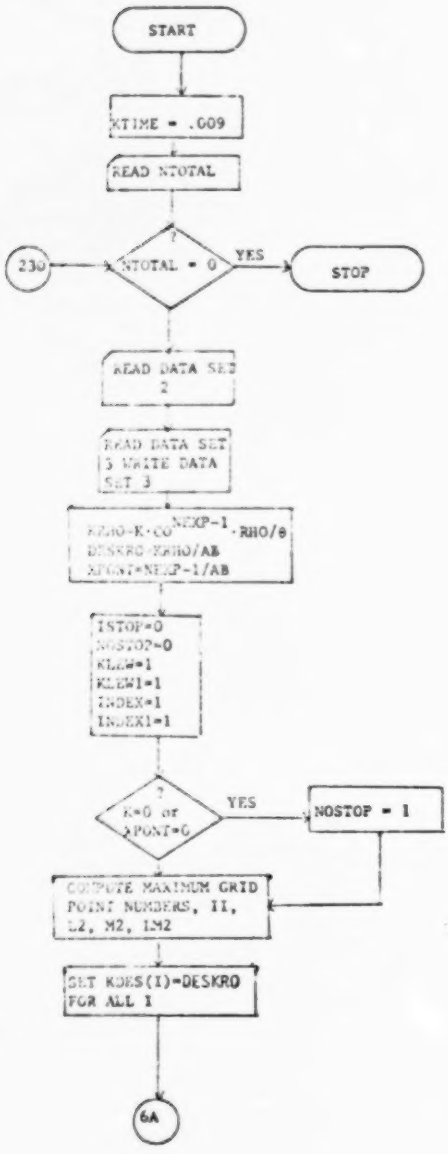
data set 2      1.          0.       1022.        0.         1.

data set 3      2.       -   .13         .4        .38       1.47
              120.         45.          0.         .9        1.0
                3.2          .03         .2

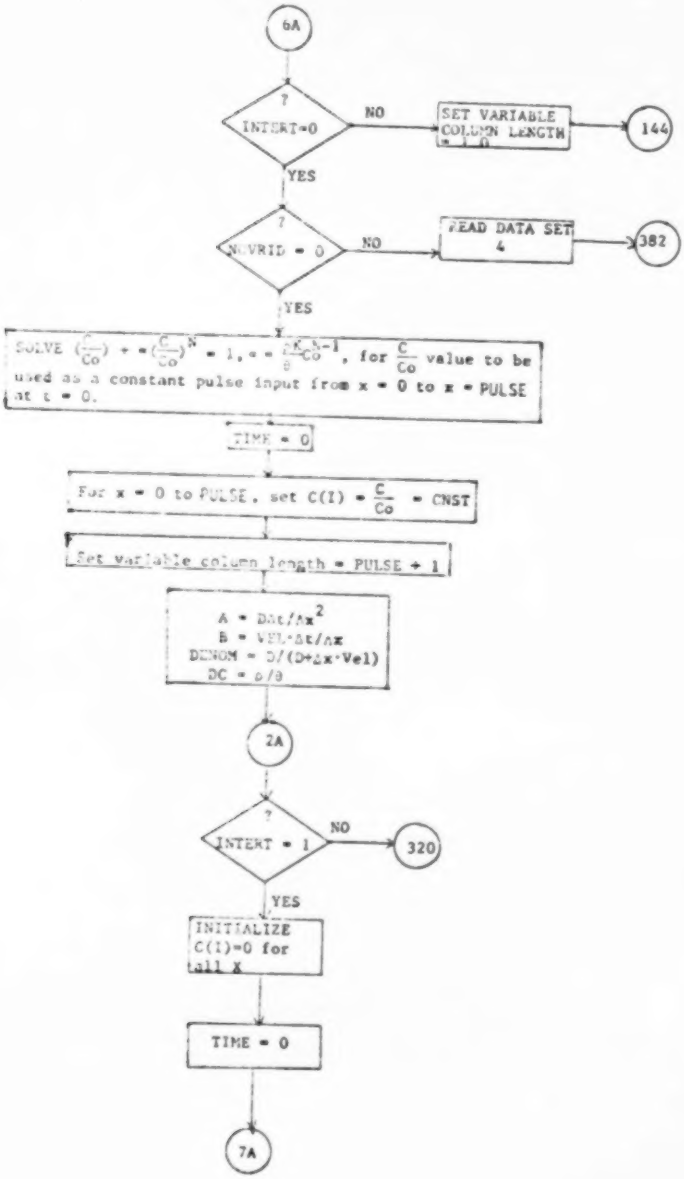
data set 4       .478

data set 5       .1        40.         30.       12.
```

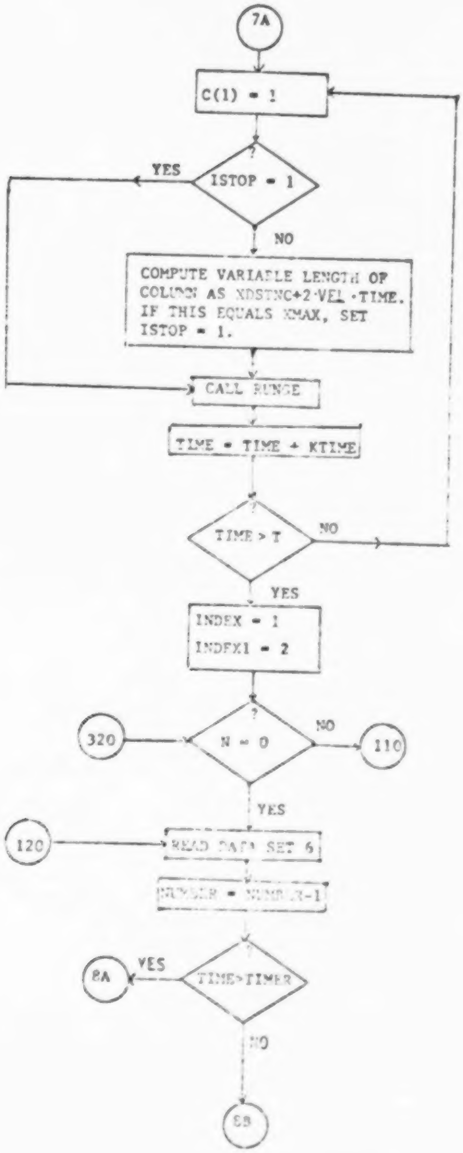
FLOW CHART FOR SOLUTE TRANSPORT PROGRAM ---
MAIN PROGRAM


START
XTIME = .009
READ NTOTAL
?
230
NTOTAL = 0
YES
STOP
READ DATA SET 2
READ DATA SET 3 WRITE DATA SET 3
KRHO=K·CO^NEXP-1·RHO/θ
DESKRO=KRHO/AB
XPONT=NEXP-1/AB
ISTOP=0
NOSTOP=0
KLEW=1
KLEW1=1
INDEX=1
INDEX1=1
?
K=0 or XPONT=0
YES
NOSTOP = 1
COMPUTE MAXIMUM GRID POINT NUMBERS, II, L2, M2, IM2
SET KDES(I)=DESKRO FOR ALL I
6A

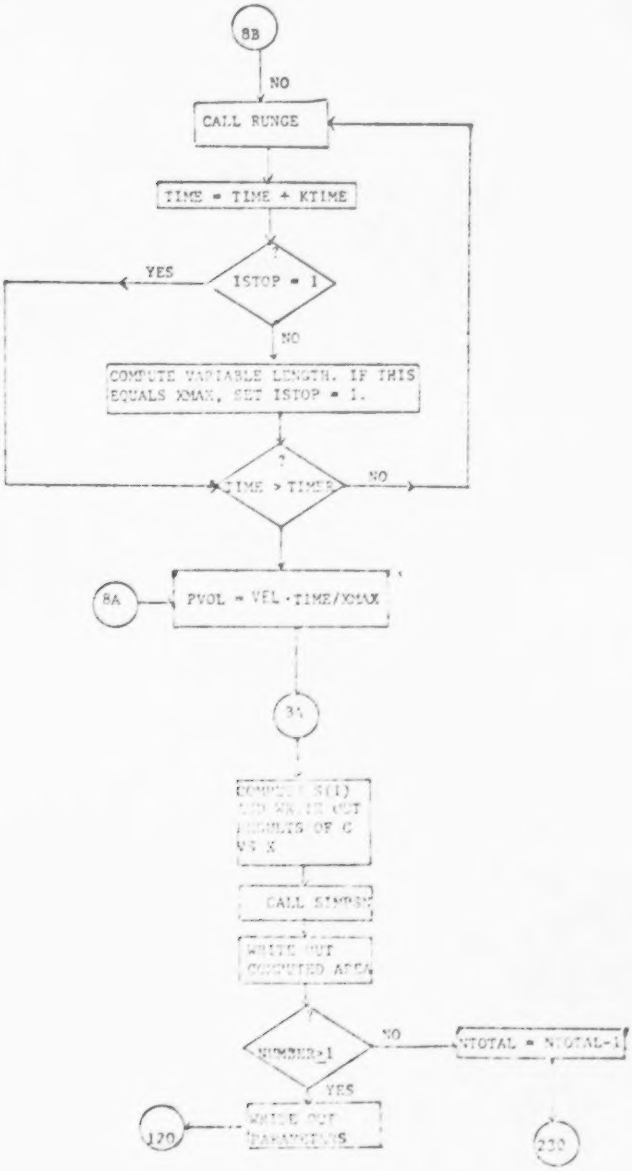
FLOW CHART FOR SOLUTE TRANSPORT PROGRAM --- MAIN PROGRAM (Continued)


6A
? INTERT=0
NO
SET VARIABLE COLUMN LENGTH = 1.0
144
YES
? NOVRID = 0
NO
READ DATA SET 4
382
YES
SOLVE $(\frac{C}{Co}) + \alpha(\frac{C}{Co})^N = 1$, $\alpha = \frac{\rho K}{\theta}Co^{N-1}$, for $\frac{C}{Co}$ value to be used as a constant pulse input from x = 0 to x = PULSE at t = 0.
TIME = 0
For x = 0 to PULSE, set C(I) = $\frac{C}{Co}$ = CNST
Set variable column length = PULSE + 1
$A = D\Delta t/\Delta x^2$
$B = VEL\cdot\Delta t/\Delta x$
$DENOM = D/(D+\Delta x\cdot Vel)$
$DC = \rho/\theta$
2A
? INTERT = 1
NO
320
YES
INITIALIZE C(I)=0 for all X
TIME = 0
7A

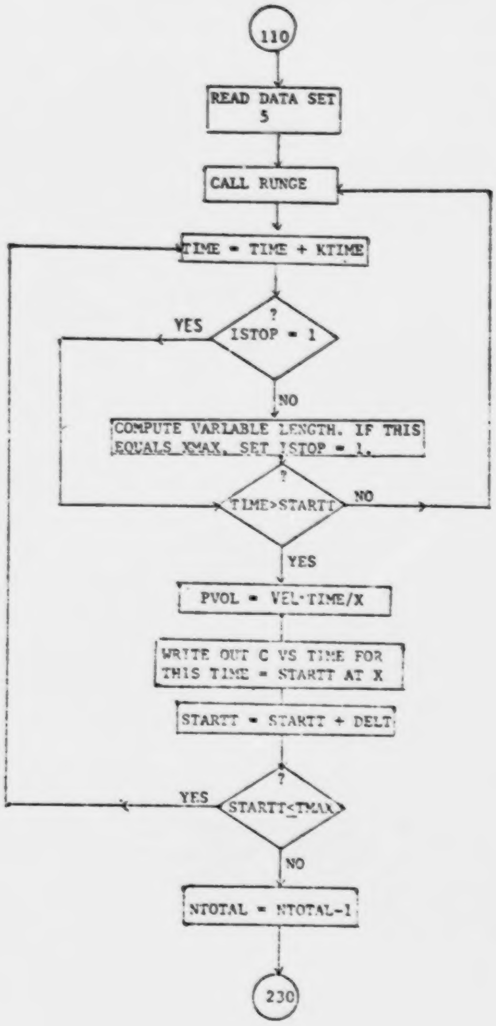
FLOW CHART FOR SOLUTE TRANSPORT PROGRAM --- MAIN PROGRAM (Continued)


7A
C(1) = 1
?
ISTOP = 1
YES
NO
COMPUTE VARIABLE LENGTH OF COLUMN AS XDSTNC+2·VEL·TIME. IF THIS EQUALS XMAX, SET ISTOP = 1.
CALL RUNGE
TIME = TIME + KTIME
?
TIME > T
NO
YES
INDEX = 1
INDEX1 = 2
320
?
N = 0
NO
110
YES
120
READ DATA SET 6
NUMBER = NUMBER-1
?
8A
YES
TIME>TIMER
NO
8B

FLOW CHART FOR SOLUTE TRANSPORT PROGRAM --- MAIN PROGRAM (Continued)

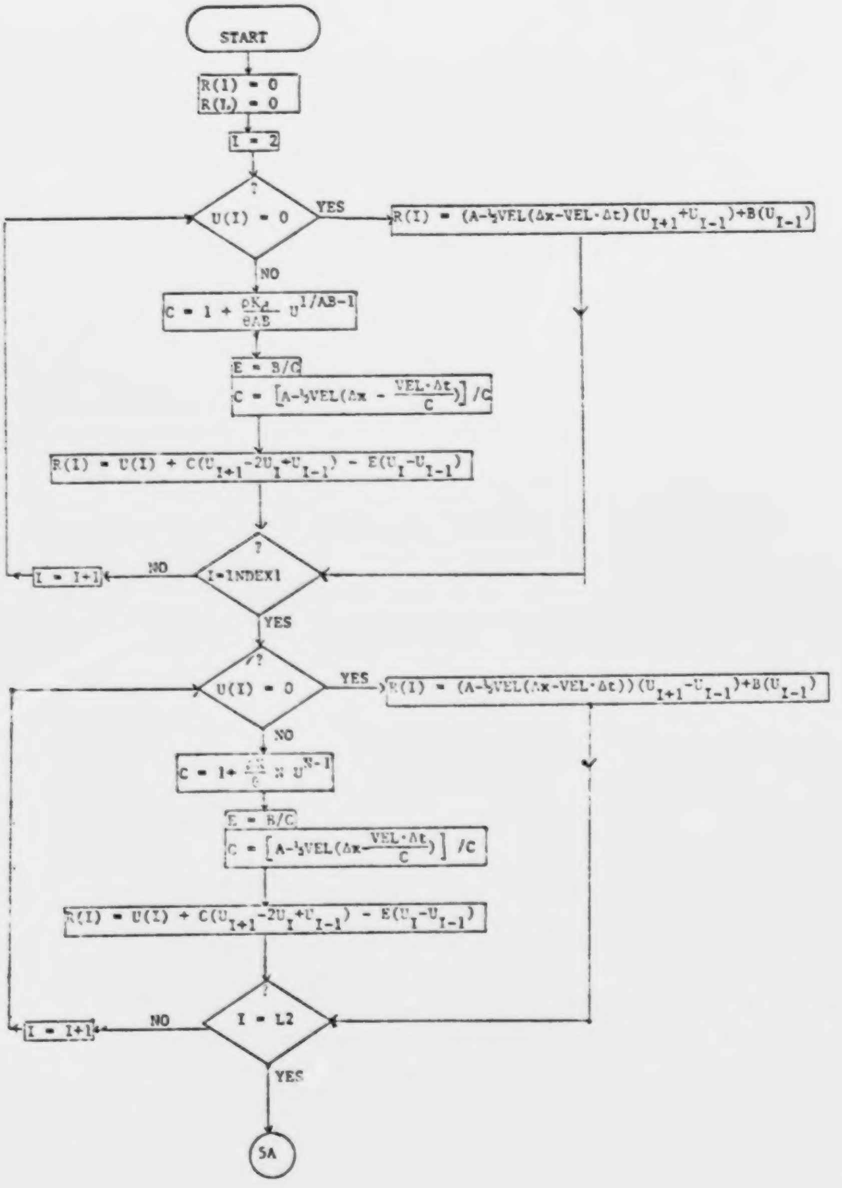

8B
NO
CALL RUNGE
TIME = TIME + KTIME
?
ISTOP = 1
YES
NO
COMPUTE VARIABLE LENGTH. IF THIS EQUALS XMAX, SET ISTOP = 1.
?
TIME > TIMER
NO
8A
PVOL = VEL·TIME/XMAX
3A
COMPUTE S(I) AND WRITE OUT RESULTS OF C VS X
CALL SIMPSN
WRITE OUT COMPUTED AREA
?
NUMBER≥1
NO
NTOTAL = NTOTAL-1
YES
WRITE OUT PARAMETERS
120
230

FLOW CHART FOR SOLUTE TRANSPORT PROGRAM --- MAIN PROGRAM (Continued)

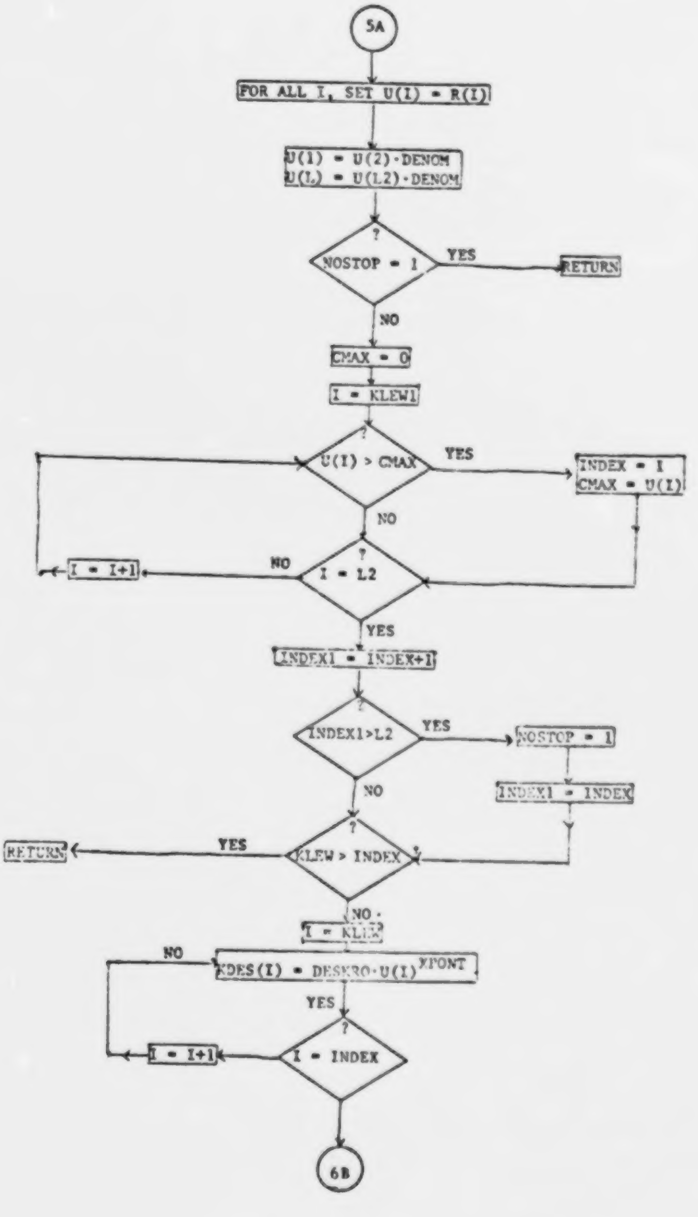


110
READ DATA SET 5
CALL RUNGE
TIME = TIME + KTIME
? ISTOP = 1
YES
NO
COMPUTE VARIABLE LENGTH. IF THIS EQUALS XMAX, SET ISTOP = 1.
? TIME>STARTT
NO
YES
PVOL = VEL·TIME/X
WRITE OUT C VS TIME FOR THIS TIME = STARTT AT X
STARTT = STARTT + DELT
? STARTT≤TMAX
YES
NO
NTOTAL = NTOTAL-1
230

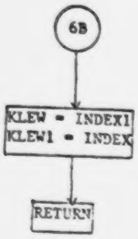
FLOW CHART FOR SOLUTE TRANSPORT PROGRAM --- RUNGE SUBROUTINE


START
R(I) = 0
R(L) = 0
I = 2
?
U(I) = 0
YES
$R(I) = (A - \frac{1}{2}VEL(\Delta x - VEL \cdot \Delta t)(U_{I+1} + U_{I-1}) + B(U_{I-1})$
NO
$C = 1 + \frac{\rho K_d}{\theta AB} U^{1/AB-1}$
E = B/C
$C = [A - \frac{1}{2}VEL(\Delta x - \frac{VEL \cdot \Delta t}{C})]/C$
$R(I) = U(I) + C(U_{I+1} - 2U_I + U_{I-1}) - E(U_I - U_{I-1})$
?
I=INDEX1
NO
I = I+1
YES
?
U(I) = 0
YES
$R(I) = (A - \frac{1}{2}VEL(\Delta x - VEL \cdot \Delta t))(U_{I+1} - U_{I-1}) + B(U_{I-1})$
NO
$C = 1 + \frac{\rho K}{\theta} N U^{N-1}$
E = B/C
$C = [A - \frac{1}{2}VEL(\Delta x - \frac{VEL \cdot \Delta t}{C})]/C$
$R(I) = U(I) + C(U_{I+1} - 2U_I + U_{I-1}) - E(U_I - U_{I-1})$
?
I = L2
NO
I = I+1
YES
5A

FLOW CHART FOR SOLUTE TRANSPORT PROGRAM — RUNGE SUBROUTINE (Continued)


5A
FOR ALL I, SET U(I) = R(I)
U(1) = U(2)·DENOM
U(L) = U(L2)·DENOM
?
NOSTOP = 1
YES
RETURN
NO
CMAX = 0
I = KLEW1
?
U(I) > CMAX
YES
INDEX = I
CMAX = U(I)
NO
?
I = L2
NO
I = I+1
YES
INDEX1 = INDEX+1
?
INDEX1>L2
YES
NOSTOP = 1
INDEX1 = INDEX
NO
?
KLEW > INDEX
YES
RETURN
NO
I = KLEW
NO
KDES(I) = DESKRO·U(I)^XPONT
YES
?
I = INDEX
I = I+1
6B

FLOW CHART FOR SOLUTE TRANSPORT PROGRAM --- RUNGE SUBROUTINE (Continued)


6B
KLEW = INDEX1
KLEW1 = INDEX
RETURN

SUBROUTINE SIMPSN MERELY INTEGRATES $\int C \cdot dx$ and $\int S \cdot dx$ USING THE TRAPEZOIDAL INTEGRATION RULE.

$$\int C \cdot dx = \frac{\Delta x}{2} \left[C(1) + 2C(2) + 2C(3) + \ldots + 2C(L2) + C(L) \right]$$

SOLUTE TRANSPORT PROGRAM

```
C
C     PROGRAM TO COMPUTE CHEMICAL CONCENTRATIONS IN SOLUTION AND ON THE
C     SOIL FOR A STEADY STATE CONSTANT FLUX SOIL-WATER SYSTEM.  THIS IS
C     THE MAIN PROGRAM WHICH ONLY CONTROLS BUT DOES NOT ACTUALLY
C     CALCULATE C.
C
C     RUNGE = SUBROUTINE USED FOR CALCULATIONS OF C AND S.
C     SIMPSN= SUBROUTINE USED TO CALCULATE THE AREA FOR C VS X RUNS ONLY.
C     C= RELATIVE CONCENTRATION
C     S= SORBED VALUES
C     NEXP= THE CONSTANT EXPONENT ON THE TERM C**N, NEXP=N
C     AB= THE CONSTANT IN THE EXPONENT ON THE TERM C**(1/AB) USED FOR
C           DESORPTION
C     CO= THE MAGNITUDE OF THE INPUT PULSE
C     VEL=VELOCITY
C     RHO= BULK DENSITY OF SOIL
C     THETA= VOLUMETRIC WATER CONTENT
C     K= THE CONSTANT K FOR ABSORPTION
C     KRHO= THE CONSTANT K MODIFIED SO THAT KRHO*(U**N)=K*(C**N) WHERE
C        U= C/CO.
C     KDES= THE DESORPTION K, MODIFIED AS KRHO.
C     D= DIFFUSION COEFFICIENT
C     KTIME= THE TIME INCREMENT USED IN THE CALCULATIONS.  THIS WILL BE
C        A CONSTANT FOR ALL PROGRAMS, AND IS NOT TO BE CONFUSED WITH DELT
C     H= THE SPATIAL INCREMENT, SIMILAR IN USE TO KTIME, USUALLY EQUAL
C        TO .2, NOT TO BE CONFUSED WITH DELX.  CAN'T BE LESS THAN .1.
C     T= PERIOD FOR WHICH CO IS TO BE APPLIED.
C     TMAX= THE MAXIMUM TIME UNDER STUDY THAT WATER IS TO BE APPLIED TO
C        THE SOIL SYSTEM.
C     DELT= INCREMENTAL TIME FOR WHICH SAMPLES ARE TO BE TAKEN.  FOR
C        EVERY DELT A VALUE OF C WILL BE PRINTED.
C     STARTT= THE STARTING TIME FOR THE BEGINNING OF THE DELT PRINT-
C        OUTS, USED ONLY FOR CONSTANT X RUNS, MUST BE GREATER THAN T.
C     XMAX= MAXIMUM DISTANCE INTO SOIL SURFACE, IN CM, MUST BE A  MULTI-
C        PLE OF H, CANNOT BE GREATER THAN 60 WITHOUT FURTHER DIMENSIONING.
C     DELX= INCREMENT OF DEPTH AT WHICH SAMPLES ARE TO BE TAKEN, MUST BE
C        A MULTIPLE OF AND GREATER THAN H, USED FOR CONSTANT TIME RUNS
C        ONLY.
C
C     NTOTAL= TOTAL NUMBER OF TIMES THE PROGRAM IS TO BE RUN.
C     N: FOR  EACH RUN, IF N=1, X IS HELD CONSTANT, TIME IS VARIED;
C                       IF N=0, TIME IS HELD CONSTANT, X IS VARIED.
C
C     NUMBER= TO BE USED ONLY FOR CONSTANT X RUNS.  THIS TELLS THE TOTAL
C        NUMBER OF DIFFERENT TIMES DURING THE RUN THAT THE X VALUES ARE
C        TO BE PRINTED OUT.  IF ONLY TMAX IS USED FOR THE RUN, THIS NUM-
C        BER MAY BE ENTERED AS A ONE OR MAY BE LEFT BLANK.
C
C     INTERT= IF THE PULSE IS ALREADY IN THE COLUMN AT TIME=0, SET
C        INTERT=0 AND READ IN THE PULSE LENGTH.  THE PROGRAM WILL CALCU-
C        LATE THE INITIAL VALUES OF C AND S USING C=1-RHO*K/THETA*C**N
C        AND RHO*S/THETA=1, WHERE S AND C ARE RELATIVE CONCENTRATIONS.
C        IF THE PROGRAM IS TO ENTER THE PULSE, SET INTERT=1 AND SPECIFY T.
C
C     PULSE= THE DISTANCE, IN CM, OF THE INITIAL CHEMICAL DISTRIBUTION
C        WHEN THE CHEMICAL IS INITIALLY DISTRIBUTED THROUGHOUT THE SOIL.
C        THE INITIAL DIST IS FROM X=0 TO X=PULSE.  THIS IS USED ONLY WHEN
C        INTERT=0.
```

SOLUTE TRANSPORT PROGRAM (Continued)

```
C
      DOUBLE PRECISION X
      REAL K,KTIME,NEXP,KRHO,KDES
      DIMENSION C(802),S(802),KDES(802)
      COMMON /BLOK1/C,S/BLOK2/KTIME,H,A,B,DC,DENOM,SMAX,ANT,AX
      COMMON /BLOK3/L2,INDEX,INDEX1,LM2
      COMMON /BLOK4/KDES,KLEW,DESKRO,XPONT,KLEW1,VELK,DN
      IE=12
      READ(5,10) NTOTAL
  230 IF(NTOTAL .LE. 0) STOP
C
C     IF N=1, NUMBER NEED NOT BE SPECIFIED
C
      READ(5,10) N,NUMBER,IXXX,INTERT,NOVRID
      W=N
      WRITE(6,10) IXXX
C
C     IF INTERT=0, ENTER A PULSE VALUE, ELSE LEAVE BLANK
C
      READ(5,20) VEL,D,K,THETA,RHO,CO,XMAX,T,NEXP,AB,PULSE,KTIME,H
      WRITE(6,30) VEL,D,K,KTIME,THETA,RHO,T,CO,AB,NEXP,H
C
C     INITIALIZE CONSTANTS AND CONTROL VARIABLES
      ISTOP=0
      NOSTOP=0
      TLD= KTIME
      DAY= KTIME/.009
      KTIME= .009000000
      KLEW=1
      KLEW1=1
      IF(K .LT. 1.E-14) NOSTOP=1
      A1=VEL
      A2=T
      A4=D
      KRHO= K*CO**(NEXP-1.)*RHO/THETA
      DESKRO= KRHO/AB
      AX= NEXP-1.
      KRHO= KRHO*NEXP
      XPONT= NEXP-1./AB
      DXP= ABS(XPONT)
      IF(DXP .LT. 1.E-14) NOSTOP=1
  515 INDEX=1
      INDEX1=2
      ANT= 1./AB-1.
      VEL=VEL*DAY
      T=T/DAY
      IF(DXP .LT. 1.E-60) XPONT= 1.E-60
      IF((ANT .LT. 1.E-60) .AND. (ANT .GT. -1.E-60)) ANT= 1.E-60
      IF((AX  .LT. 1.E-60) .AND. (AX  .GT. -1.E-60)) AX = 1.E-60
      II=XMAX/H+2.+.01*H
      L2=II-1
      M2= L2
      LM2= II-2
      DO 600 I=1,II
  600 KDES(I)= DESKRO
      D=A4*DAY
      TAME= .1*KTIME
      IF(INTERT) 380,380,390
  390 NOT=0
```

SOLUTE TRANSPORT PROGRAM (Continued)

```
      XDSTNC= 4.01*H
      GO TO 144
  380 IF(NOVRID) 381,381,389
  389 READ(5,20) CNST
      GO TO 382
  381 BETA= RHO*K/THETA*(CO**(NEXP-1.))
      CNST= 1./(1.+RHO*K/THETA)
      MEMORY=1
      Z= 1./CNST
  387 Z= 1.+BETA*Z**(1.-NEXP)
      CNST= 1./Z
      XY= CNST+BETA*CNST**NEXP
      IF(ABS(XY-1.00) .LT. .0005) GO TO 382
      IF(MEMORY .GE. 100) GO TO 383
      MEMORY= MEMORY+1
      GO TO 387
  383 WRITE(6,388) K,NEXP,CO,RHO,THETA,CNST
      IF((CNST .GT. 1.00) .OR. (CNST .LT. 0.0)) GO TO 384
      WRITE (6,386)
      GO TO 382
  384 WRITE(6,391)
      STOP
  382 TIME=0
      MP=PULSE/H +1.+.1*H
      NP=MP+1
      DO 222 J=1,MP
  222 C(J)= CNST
      DO 223 J=NP,II
  223 C(J)= 0
      NOT=1
      XDSTNC= PULSE+4.01*H
      DSTNCE= XDSTNC
      II= XDSTNC/H+2.0
      L2=II-1
      LM2= II-2
C
C     COMPUTE SOME CONSTANTS TO BE USED IN SUBROUTINE RUNGE
C
  144 A= D/H/H*KTIME
      B= VEL/H*KTIME
      DN= .5*VEL*KTIME/H/H
      VELK= VEL*KTIME
      DENOM= D/(D+H*VEL)
      DC=RHO/THETA
      IF(NOT) 330,330,320
C
C     PUT THE PULSE OF CO IN FOR A TIME T
C
  330 DO 40 J=1,II
   40 C(J)=0
      TIME=0
   70 C(1)=1.
      IF(ISTOP) 520,520,530
  520 DSTNCE= VEL*TIME*2.+XDSTNC
      IF(DSTNCE-XMAX) 540,550,550
  550 ISTOP=1
      II= XMAX/H+2.0
      GO TO 560
  540 II=DSTNCE/H+2.0
  560 L2=II-1
      LM2= II-2
  530 CALL RUNGE(II,KRHO,NOSTOP)
      TIME=TIME+KTIME
      IF(TIME+TAME .GE. T) GO TO 310
      GO TO 70
  310 NOT=10
      INDEX=1
      INDEX1=2
C
C     IF N=1, READ IN DELT,TMAX,X,STARTT
C     IF N=0, READ IN DELX,TIMER
C
  320 IF(N) 120,120,110
C
C     STATEMENT 120 IS FOR CONSTANT TIME
C
  120 READ(5,20) DELX,TIMER
      INT=DELX/H+.01*H
      IF (INT .LE. 0) INT=1
C
C     IF NUMBER >1, THEN PUNCH NUMBER CARDS, EACH WITH ONE VALUE OF TIME
C     IN HOURS ON IT FOR WHICH TIME VALUES OF C VS X WILL BE PRINTED
C
      TIMER=TIMER/DAY
  140 NUMBER=NUMBER-1
      IF(TIME+TAME .GE. TIMER) GO TO 160
  150 CALL RUNGE(II,KRHO,NOSTOP)
      TIME=TIME+KTIME
      IF(ISTOP) 400,400,410
  400 DSTNCE= VEL*TIME*2.+XDSTNC
      IF(DSTNCE-XMAX) 420,430,430
  430 ISTOP=1
      II= XMAX/H+2.0
      GO TO 440
  420 II= DSTNCE/H+2.0
  440 L2= II-1
      LM2= II-2
  410 IF(TIME .LT. TIMER) GO TO 150
  160 PVOL=VEL*TIME/XMAX
      WRITE(7,10) IXXX
      WRITE(7,340) H,A1,RHO,THETA,A2,CO,K,CO
      WRITE(7,341) A4,PVOL,IE,CO,AB,NEXP
C
C     WRITE OUT THE C AND S VS X VALUES
C
      DO 171 J=1,M2
      IF(J .GE. INDEX) GO TO 363
      S(J)= KDES(J)*AB*C(J)**(1./AB)
      GO TO 171
  363 S(J)= KRHO/NEXP*C(J)**NEXP
  171 CONTINUE
      DO 170 J=1,M2,INT
      IF(J .EQ. M2) GO TO 180
  190 IF(C(J) .LT. 1.E-6) GO TO 170
  180 X=J-1
  370 X=H*X
      TIMM=TIME*DAY
      WRITE(7,20) X,C(J),S(J)
```

SOLUTE TRANSPORT PROGRAM (Continued)

```
      WRITE(6,210) TIMM,X,PVOL,C(J),S(J)
  170 CONTINUE
      CALL SIMPSN(SUMS,SUMC,SUM,M2,H,DC)
      WRITE(6,82) SUMC,SUMS,SUM
      IF(NUMBER .GE. 1) GO TO 125
  220 NTOTAL =NTOTAL-1
      WRITE(6,172)
      GO TO 230
  125 WRITE(6,30) A1,A4,K,TLD,THETA,RHO,A2,CO,AB,NEXP,H
      GO TO 120
C
C     STATEMENT 110 IS FOR CONSTANT X
C     X IS THE X VALUE AT WHICH THE SAMPLES ARE TO BE TAKEN
C
  110 READ(5,20) DELT,TMAX,X,STARTT
      WRITE(7,10) IXXX
      WRITE(7,340) W,A1,RHO,THETA,A2,CO,K,CO
      WRITE(7,341) A4,X,IE,CO,AB,NEXP
      STARTT=STARTT/DAY
      DELT=DELT/DAY
      TMAX=TMAX/DAY
      INT=X/H+1.+.01*H
  240 CALL RUNGE(II,KRHO,NOSTOP)
      TIME=TIME+KTIME
      IF(ISTOP) 450,450,460
  450 DSTNCE= VEL*TIME*2.+XDSTNC
      IF(DSTNCE-XMAX) 470,480,480
  480 ISTOP= 1
      II= XMAX/H+2.0
      GO TO 490
  470 II= DSTNCE/H+2.0
  490 L2= II-1
      LM2= II-2
  460 IF(TIME+TAME .LT. STARTT) GO TO 240
C
C     WRITE OUT THE C AND S VS TIME VALUES
C
  250 IF(C(INT) .LT. 1.E-6) GO TO 260
  270 PVOL= VEL*TIME/X
      TIMM=TIME*DAY
      IF(INT .GE. INDEX) GO TO 314
      SS= KDES(INT)*AB*C(INT)**(1./AB)
      GO TO 317
  314 SS= KRHO/NEXP*C(INT)**NEXP
  317 WRITE(6,210) TIMM,X,PVOL,C(INT),SS
      WRITE(7,20) PVOL,C(INT)
  260 STARTT=STARTT+DELT
      IF(STARTT .LE. TMAX) GO TO 240
      PVOL=0
      WRITE(7,20) PVOL, PVOL
      NTOTAL=NTOTAL-1
      WRITE(6,172)
      GO TO 230
  300 STOP
   10 FORMAT(6I5)
   20 FORMAT(5F15.5)
   30 FORMAT(1X,//,5X,'VEL=',E10.3,5X,'D=',E10.3,5X,'K=',E11.3,5X,
     *'KTIME=',E10.3,5X,'THETA=',E10.3,/5X,'RHO=',E10.3,5X,'T=',E10.3,
     *5X,'CO=',E10.3,8X,'AB=',E10.3,6X,'NEXP=',E10.3,5X,'DELX, H=',E10.3
     * ,///,20X,'TIME',18X,'X',14X,'PORE VOLUME',21X,'C/CO',11X,'RHO*S/C
     *O*THETA')
  82  FORMAT(1X,'THE TOTAL AMOUNT OF CONCENTRATION, C, PRESENT IS, ',
     5'C=',F10.3,/,1X,'THE TOTAL AMOUNT OF CONCENTRATION, S, PRESENT ',
     *'IS, S=',F10.3,/,'+',T54,'__________',/,1X,'THE SUM OF S AND C IS,
     * RHO*S/CO*THETA + C=',T54,F10.3,////)
 172 FORMAT(1H1)
 210 FORMAT(17X,3(F10.5,10X),2E20.4)
 340 FORMAT(1X,F9.3,7F10.3)
 341 FORMAT(2F10.3,I2,3F10.3)
 386 FORMAT(5X,/,5X,'SINCE C/CO, AFTER 100 ITERATIONS, IS .GT. 0 AND .L
     *T. 1.0, THE CALCULATIONS WILL PROCEED USING THIS VALUE.',/)
 388 FORMAT(1X,/,5X,'FOR THE PARAMETERS: K=',F12.4,', NEXP=',F12.4,', C
     *O=',F12.4,', RHO=',F12.4,', THETA=',F12.4,//,5X,'AND FOR AN INITIA
     *LLY DISTRIBUTED PULSE, CONVERGENCE DID NOT OCCUR ON THE ITERATIVE'
     *,/,5X,'CALCULATIONS OF THE INITIAL C/CO AND S/CO VALUES. AFTER 100
     * ITERATIONS THE VALUE OF C/CO= ',E14.7,/)
 391 FORMAT(5X,/,5X,'THE CALCULATION OF C/CO IS OUTSIDE THE ALLOWED RAN
     *GE.',/,5X,'THEREFORE, YOU MUST READ IN THE VALUE OF C/CO ON A CARD
     *. THIS CAN BE DONE BY SETTING THE VALUE OF NOVRID=1',/)
      END
```

SOLUTE TRANSPORT PROGRAM (Continued)

```
      SUBROUTINE RUNGE(L,KRHO,NOSTOP)
      REAL K,KRHO,KDES
      DIMENSION U(802),S(802),R(802),KDES(802)
      COMMON /BLOK1/U,S/BLOK2/K,H,A,B,D,DENOM,SMAX,ANT,AX
      COMMON /BLOK3/ L2,INDEX, INDEX1,LM2
      COMMON /BLOK4/KDES,KLEW,DESKRC,XPONT,KLEW1,VELK,DN
C
C     CALCULATES NEW VALUES OF C AND S USING THE PREVIOUS OLD VALUES.
C     K IS THE TIME INCREMENT
C
      R(1)= 0
      R(L)=  0
      DO 30 I=2,INDEX1
      IF(U(I)) 40,40,50
   40 R(I)= (A-DN*(H-VELK))*(U(I-1)+U I+1))+B*U(I-1)
      GO TO 30
   50 C= 1.+KDES(I)*U(I)**ANT
      E= B/C
      C= (A-DN*(H-VELK/C))/C
      R(I)= U(I)+(C*(U(I-1)-2.*U(I)+U(I+1))-E*(U(I)-U(I-1)))
   30 CONTINUE
      DO 100 I=INDEX,L2
      IF(U(I)) 10,10,20
   10 R(I)= (A-DN*(H-VELK))*(U(I-1)+U(I+1))+B*U(I-1)
      GO TO 100
   20 C= 1.+KRHO*U(I)**AX
      E= B/C
      C= (A-DN*(H-VELK/C))/C
      R(I)= U(I)+(C*(U(I-1)-2.*U(I)+U(I+1))-E*(U(I)-U(I-1)))
  100 CONTINUE
      DO 130 I=2,L2
      U(I)= ABS(R(I))
  130 CONTINUE
      U(1)= ABS(U(2)*DENOM)
      U(L)= ABS(U(L2)*DENOM)
      IF(NOSTOP .EQ. 1) RETURN
      CMAX=0
      DO 60 I=KLEW1,L2
      IF(U(I)-CMAX) 60,60,110
  110 INDEX=I
      CMAX=U(I)
   60 CONTINUE
      INDEX1= INDEX+1
      IF(INDEX1 .GT. L2) NOSTOP=1
      IF(INDEX1 .GT. L2) INDEX1= INDEX
      IF(KLEW .GT. INDEX) RETURN
      DO 140 I=KLEW,INDEX
  140 KDES(I)= DESKRO*U(I)**XPONT
      KLEW= INDEX1
      KLEW1= INDEX
  260 RETURN
      END
      SUBROUTINE SIMPSN(SUMS,SUMC,SUM,II,H,DC)
      DIMENSION C(602),S(602)
      COMMON /BLOK1/C,S
C
C     INTEGRATES S/CO AND C/CO FOR OUTPUT VALUES FROM MAIN PROGRAM USING
C     RECTANGULAR INTEGRATION.
C
      SUMC=0.
      SUMS=0.
   40 DO 13 NODD= 2,II
      IF(NODD-II) 50,13,13
   50 SUMS= SUMS+2.*S(NODD)
      SUMC= SUMC+2.*C(NODD)
   13 CONTINUE
      SUMS= H/2.*(SUMS+S(1)+S(II))
      SUMC= H/2.*(SUMC+C(1)+C(II))
      SUM=SUMS+SUMC
      RETURN
      END
```

APPENDIX B

Computer Program for Simulating Simultaneous Movement of Water and Solute through Soils

INPUT-OUTPUT

DATA FORMAT

The following details the input data. Each data set represents a READ statement in the program. Some data sets are required, others are dependent upon other input variables read in. Do these in order unless otherwise directed.

DATA SET 1: FORMAT (15) Required (read in from MAIN program)

Read NTOTAL

NTOTAL = Total number of runs to be made, each run describing its own soil system.

DATA SET 2: FORMAT (15) Required (read in from subroutine FLTRAT)

Read NMAX

NMAX = Number of tabulated values in TTABLE, HTABLE, and KTABLE

DATA SET 3: FORMAT (5F15.5) Required (read in from subroutine FLTRAT)

Read KTIME, THETAX, THETAT, HNOUTO, HNOUTN, THETAN, KOND, DELX, H, XMAX, COND, THESAT, TINC, SPEED, SURFLX, REDIST, EVAPOR, TIMEVP, TLIMIT, PULSE, SMALLT

KTIME= The time increment used in the chemical portion of the program.

THETAX= θ at $t=0$, used for constant initial conditions on θ.

THETAT= θ at $x=0$, either this represents a constant boundary condition or the boundary condition approached at $t \rightarrow \infty$ for constant flux runs.

HNOUTO= H at $x=0$, corresponds to THETAT.

HNOUTN= H at x=XMAX, corresponds to THETAN.

THETAN= θ at x=XMAX, will always be a constant.

KOND= Conductivity at $x=0$, corresponds to THETAT.

DELX= The Δx used in the infiltration calculations.

H= The Δx used in the chemical calculations. This must be an integer multiple of DELX.

XMAX= The maximum depth of the soil. The water front should never reach XMAX.

COND= Saturated conductivity for the soil.

THESAT= The saturated value of theta.

TINC= The time increment at $t=0$ for subroutine FLTRAT. The Δt will be increased automatically for these conditions: a) constant theta at the surface, or b) evaporation, or c) redistribution. The Δt will remain at TINC for constant flux runs.

SPEED= The estimated speed of the wetting front at t=0. If no estimate is available, set SPEED very large.

SURFLX= For ponded runs, set SURFLX=0. For a surface flux distribution at x=0, set SURFLX=-1.

REDIST= The cumulative infiltration at which time either redistribution or evaporation will start. If neither evaporation or redistribution is desired, set REDIST=0. If for evaporation you would rather start evaporation at some TIMEVP, set REDIST=0.

EVAPOR= The evaporation rate during evaporation. This must be negative. If no evaporation is desired, set EVAPOR=0.

TIMEVP= For evaporation, if evaporation is to start at t= TIMEVP, specify TIMEVP. For no evaporation, or if evaporation is to start according to a REDIST specification, set TIMEVP=0.

TLIMIT= The upper limit on Δt for infiltration. If no upper limit is desired, set TLIMIT=0. (This is programmed because sometimes Δt increases from, for example, 10^{-5} to 1.0 hours, and you may want to limit this.)

PULSE= If PULSE≠0, PULSE represents the distance from x=0 to x=PULSE, and for x≤PULSE, initial values of theta(x) have to be read in on cards. For x≥PULSE, theta(x) initial=THETAX. For constant initial conditions throughout, set PULSE=0.

SMALLT= For evaporation or redistribution runs, theta at x=0 will never fall below SMALLT.

(NOTE: The PULSE in data set 3 is for infiltration only, and should not be confused with the PULSE mentioned in data set 10 which is for the chemical.)

(NOTE: The DELX in data set 3 should not be confused with the DELX in data set 15).

DATA SET 4: FORMAT (5F15.5) Required (read in from subroutine FLTRAT)

Read TTABLE

TTABLE= Table of theta values in θ vs H data. There will be NMAX of these. Read in smallest value first in monotonic increasing order.

DATA SET 5: FORMAT (5F15.5) Required (read in from subroutine FLTRAT)

Read HTABLE

HTABLE= Table of H values in θ vs H data. There will be NMAX of these. Read in smallest value first in monotonic increasing order.

DATA SET 6: FORMAT (5F15.5) Required (read in from subroutine FLTRAT)

Read KTABLE

KTABLE= Table of K values in K vs θ data. There will be NMAX of these. Read in smallest value first in monotonic increasing order.

DATA SET 7: FORMAT (8F10.3) Optional (read in from subroutine FLTRAT)

If PULSE=0, go to data set 8; if PULSE>0, read data set 7.

Read THETAJ(I)

THETAJ(I)= Initial values of theta from x=0 to x=PULSE. Read in a total number of 1+PULSE/DELX values, starting from x=0.

DATA SET 8: FORMAT (415) Required (read in from MAIN program)

Read N, NUMBER, NOREAD, NOCLOR

N= For N=0, output printouts will be C vs X. For N=1, output printouts will be C vs time.

NUMBER= Use only for N=0; the number of different time values for which C vs X will be printed.

NOREAD= If NOREAD=0, the program will put a pulse in until the cumulative infiltration reaches the amount T.
If NOREAD=-1, the program will compute its own initial C values, computed from the given parameters and theta initial; C=0 for x>PULSE.
If NOREAD=+1, you are to read in on cards, 8 values of (C initial) to a card, a total of 1+PULSE/H values of C. C=0 for x>PULSE.
If NOREAD=+2, in addition to reading in C initial, also read in the same number of S initial values.

NOCLOR= If NOCLOR=1, the program will simultaneously compute a chloride run along with the regular chemical run, using the same parameters except setting K=0. If NOCLOR=0, the chloride calculations will not be made.

DATA SET 9: FORMAT (20A4) Required (read in from MAIN program)

Read NAMEIT(J)

NAMEIT(J)= One card with any type of identification desired. The information will be printed out as a heading each time C vs X or C vs time is printed. If no identification is desired, leave this card blank.

DATA SET 10: FORMAT (5F15.5) Required (read in from MAIN program)

Read D, K, RHO, T, NEXP, AB, CO, PULSE, DVS

D= Dispersion coefficient. Corrections for numerical dispersion are made within the program.

K= The absorption coefficient, $S=KC^{N}$.

RHO= The bulk density of the soil.

T= A required cumulative infiltration during which CO is applied to the soil surface. For calculated cumulative infiltration<T, CO is applied to the surface.

NEXP= The exponent N on $S=KC^{N}$.

AB= The exponent AB on $S=K_{d}C^{1/AB}$

CO= The magnitude of input chemical concentration.

PULSE= For NOREAD= +1 or +2, PULSE is the distance in the soil of an initially distributed chemical, and CLORID. For x>PULSE, C=0. If $T \neq 0$, set PULSE=0. Do not confuse this PULSE with that of data set 3.

DVS= Constant vapor diffusion coefficient, used during evaporation and redistribution to calculate the surface flux of the chemical.

DATA SET 11: FORMAT (8F10.3) Optional (read in from MAIN program)

If NOREAD= +1 or +2, execute data set 11; else go to data set 14.

Read C(J)

C(J)= Initial values of C(x) from J=1 to J=L+PULSE/H. The program assumes C(x)=0 for x>PULSE.

DATA SET 12: FORMAT (8F10.3) Optional (read in from Main program)

If NOCLOR=1, read data set 12; else go to data set 13.

Read CLORID(J)---only if C(J) also was read in.

CLORID(J)= Initial values of CLORID(x) from J=1 to J-1+PULSE/H. The program assumes CLORID(x) for x>PULSE.

DATA SET 13: FORMAT (8F10.3) Optional (read in from MAIN program)

If NOREAD=+2, read data set 13, else go to data set 14.

Read S(J)

S(J)= Initial values of S(x) from J=1+PULSE/H. The program assumes S(x)=0 for x>PULSE.

DATA SET 14: FORMAT (4F15.5) Optional (read in from MAIN program)

If N=1, read data set 14; else go to data set 15.

Read DELT, TMAX, X, STARTT

DELT= For printouts, a value of C will be printed every DELT units of time.

TMAX= For printouts, the program will halt this particular run when time=TMAX.

X= For printouts, the C value will always be printed out for the point which is a value of X down the soil profile.

STARTT= For printouts, values of C will be printed starting at time=STARTT, continuing until time=TMAX, printed every DELT.

(NOTE: If data set 14 was read, and if NTOTAL>1, control will pass to data set 2 when t=TMAX. If NTOTAL=1, the program will halt when t=TMAX).

DATA SET 15: FORMAT (2F15.5) Optional (read in from MAIN program)

If N=0, read data set 15; else go to data set 14.

Read DELX, TIMER

DELX= For printouts, at time=TIMER, C values will be printed starting at x=0 and every DELX thereafter until XMAX. Not to be confused with DELX of data set 3.

TIMER= C values will be printed vs x whenever time=TIMER.

(NOTE: Data set 15 has to be executed a total of NUMBER times.)

DATA SET 16: FORMAT (2F15.5) Optional (read in from subroutine FLTRAT)

If SURFLX=-1, read data set 16, else go to data set 2 or STOP, depending upon NTOTAL.

Read FLUX, TFLUX

FLUX= The value of surface flux to be applied at x=0 until time=TFLUX.

TFLUX= When time=TFLUX, the above value of FLUX will cease its application.

(NOTE: Data set 16 can be executed as many times as desired to get a step approximation of any surface flux distribution.)

END OF DATA SETS

EXAMPLE OF HYBRID DATA

Data Set 1	1				
Data Set 2	36				
	.02	.15	.36	0.	-1180.
Data	.15	.366	1.0	.2	56.
Set	.366	.36	.000018	13.	0.
3	4.0	-.02	5.08	.2	33.
	.03				
	.01	.02	.03	.04	.05
	.06	.07	.08	.09	.10
Data	.11	.12	.13	.14	.15
Set	.16	.17	.18	.19	.20
4	.21	.22	.23	.24	.25
	.26	.27	.28	.29	.30
	.31	.32	.33	.34	.35
	.36				
	-1120000.	-332000.	-130000.	-56000.	-31000.
	- 18800.	- 12900.	- 7950.	- 6500.	- 4800.
Data	- 3480.	- 2680.	- 2000.	- 1530.	- 1180.
Set	- 900.	- 720.	- 595.	- 495.	- 415.
5	- 350.	- 300.	- 262.	- 229.	- 200.
	- 179.	- 159.	- 138.	- 115.	- 95.
	- 75.	- 58.	- 43.	- 31.	- 22.
	0.0				

EXAMPLE OF HYBRID DATA (Cont.)

	.00000000003	.00000000006	.000000000113	.000000000216	.000000000432			
	.0000000008	.0000000016	.00000000308	.000000006	.0000000113			
Data	.0000000243	.0000000432	.0000000868	.00000017	.000000333			
Set	.00000064	.00000125	.0000024	.00000468	.000009			
6	.0000172	.0000333	.000064	.000122	.000235			
	.000452	.000884	.00172	.00333	.0066			
	.0128	.0248	.0492	.0932	.182			
	.366							
	.34	.27407	.222321	.24249	.25176	.25817	.26229	.26520
Data	.26736	.26903	.27032	.27128	.27202	.27257	.27294	.27317
Set	.27324	.27316	.27292	.27253	.27195	.27116	.27009	.26866
7	.26683	.2645	.26135	.25704	.25059	.24274	.23026	.20933
	.17637	.15276	.15					
Data Set 8	0	33		2	0			
Data Set 9	FROM PREVIOUS 48 HOUR DATA, REINFILTRATED 5 HOURS, EVAPORATED 45 HOURS-29 JAN 74							
Data Set 10		.1	.4	1.53	.475	1.0		
		2.5	90.	13.	.0			
	1.8719	1.872	2.1042	2.5	2.9063	3.343	3.7828	4.156
	4.5286	4.781	5.0337	5.194	5.3543	5.459	5.5635	5.594
Data	5.6273	5.593	5.5582	5.459	5.3596	5.201	5.042	4.83
Set	4.6174	4.379	4.1208	3.847	3.5741	3.293	3.0118	2.787
11	2.4612	2.2	1.9383	1.705	1.472	1.274	1.0752	.9158

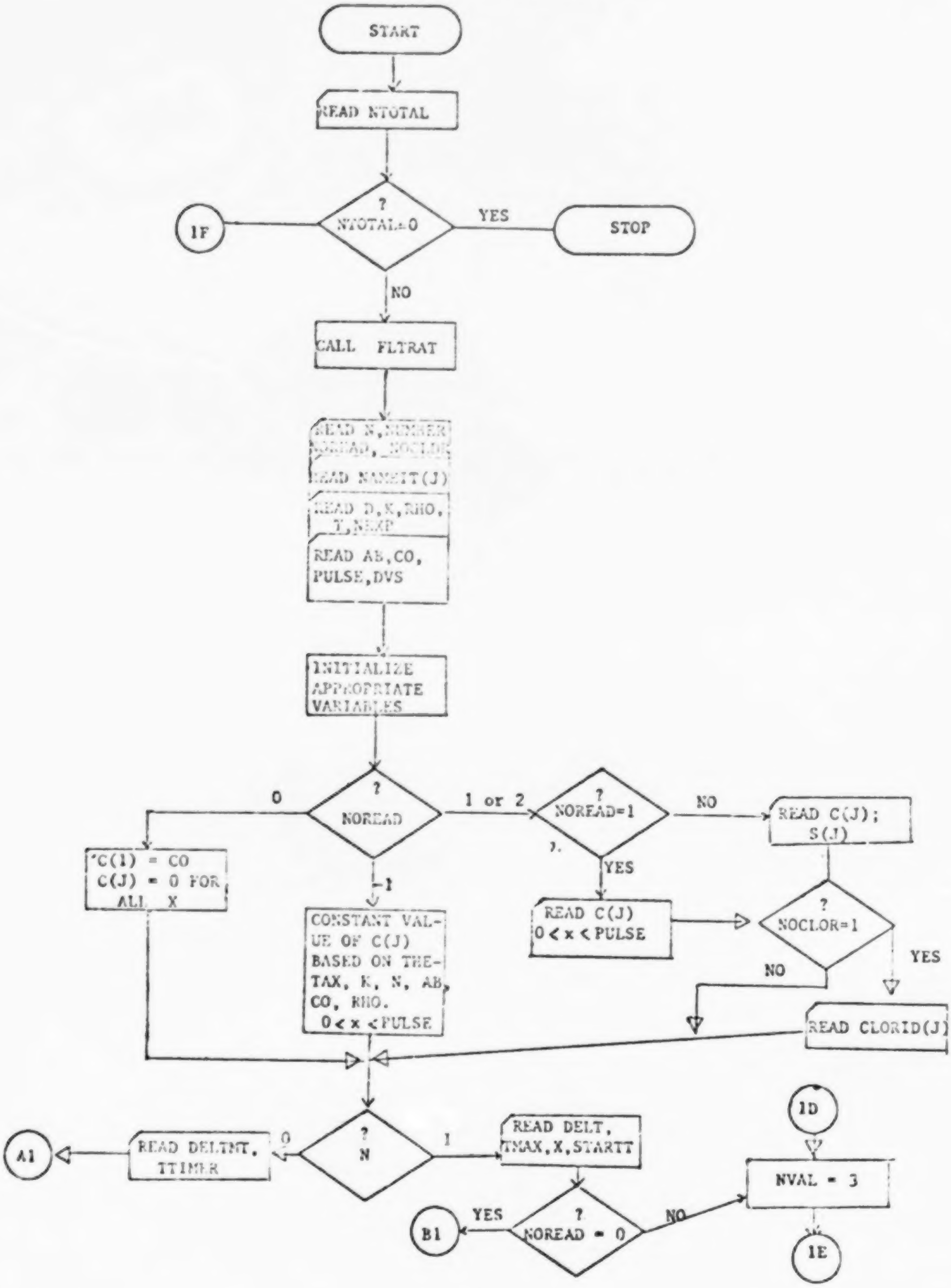
EXAMPLE OF HYBRID DATA (Cont.)

Data	.75631	.6345	.51271	.4235	.33433	.2724	.21045	.169
Set	.12758	.1011	.074606	.05837	.042135	.03254	.022945	.01752
11	.012089	.009119	.0061489	.004587	.0030247	.002232	.00144	.001051
Cont.	.00066267	.00048						
	7.6475	7.0453	6.7515	6.38585	5.8822	5.687	5.4142	5.25293
	5.0547	4.8893	4.7091	4.55356	4.3917	4.25392	4.1131	3.98067
Data	3.8484	3.72153	3.5951	3.47048	3.347	3.22347	3.1012	2.91453
Set	2.7311	2.47548	2.2225	1.96019	1.7072	1.49296	1.287	1.11479
13	.98711	.88	.77431	.682	.58882	.5096	.43009	.36632
	.30252	.2538	.20508	.1694	.13373	.10896	.084181	.0676
	.051033	.04044	.29843	.023348	.016854	.013016	.00918	.007008
	.0048356	.0036476	.0024596	.0018348	.0012099	.0008928	.0005602	.0004204
	.00026507	.000192						

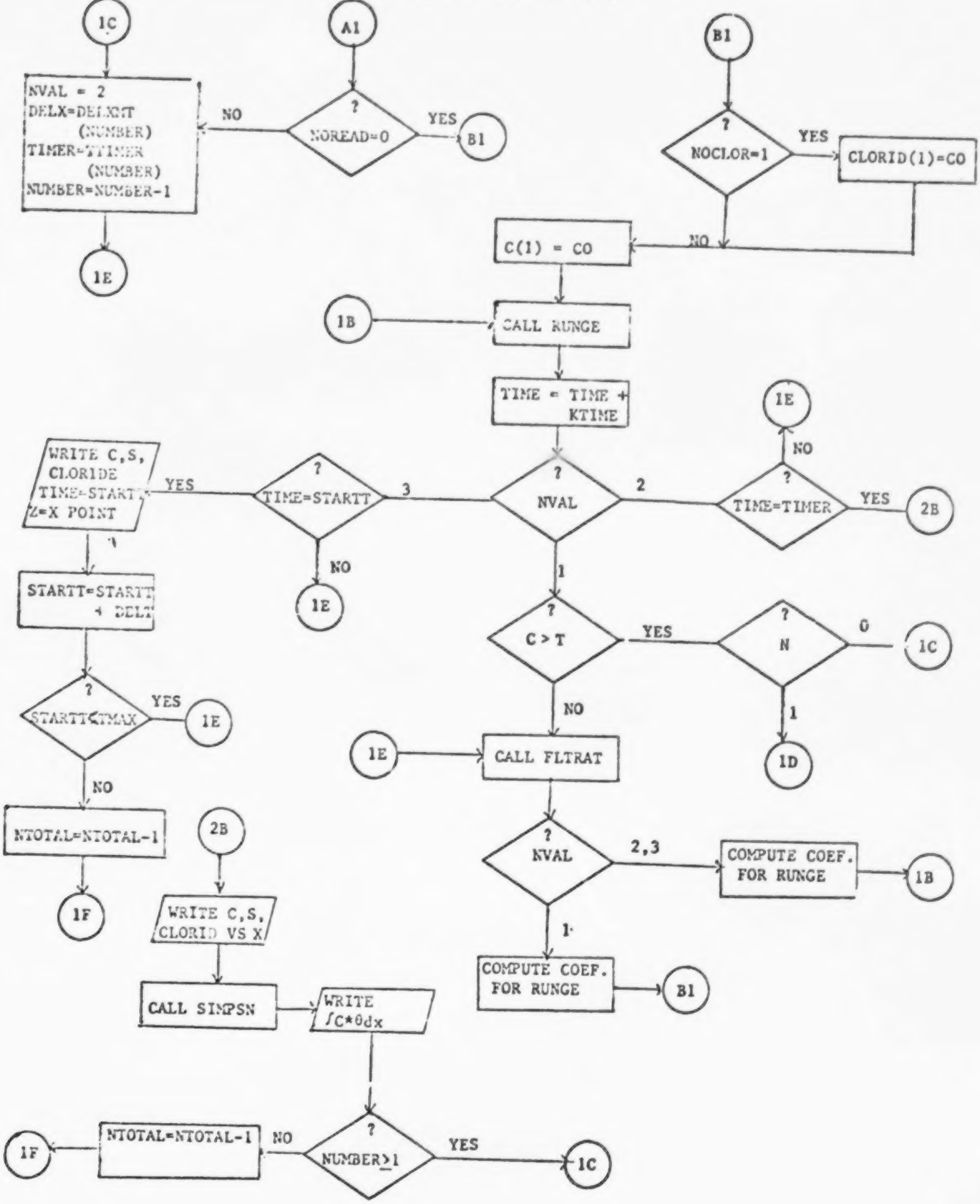
EXAMPLE OF HYBRID DATA (Cont.)

	.4	1.0
	.4	3.0
	.4	4.0
	.4	5.0
	.4	6.0
	.4	7.0
	.4	8.0
	.4	9.0
	.4	10.
	.4	11.
	.4	12.
	.4	13.
	.4	14.
Data Set 15	.4	15.
	.4	16.
	.4	17.
	.4	18.
	.4	19.
	.4	20.
	.4	21.
	.4	22.
	.4	23.
	.4	24.
	.4	25.
	.4	27.
	.4	30.
	.4	33.
	.4	36.
	.4	39.
	.4	42.
	.4	45.
	.4	48.
	.4	50.

FLOW CHART FOR SIMULTANEOUS TRANSPORT OF WATER AND SOLUTE PROGRAM -- MAIN PROGRAM

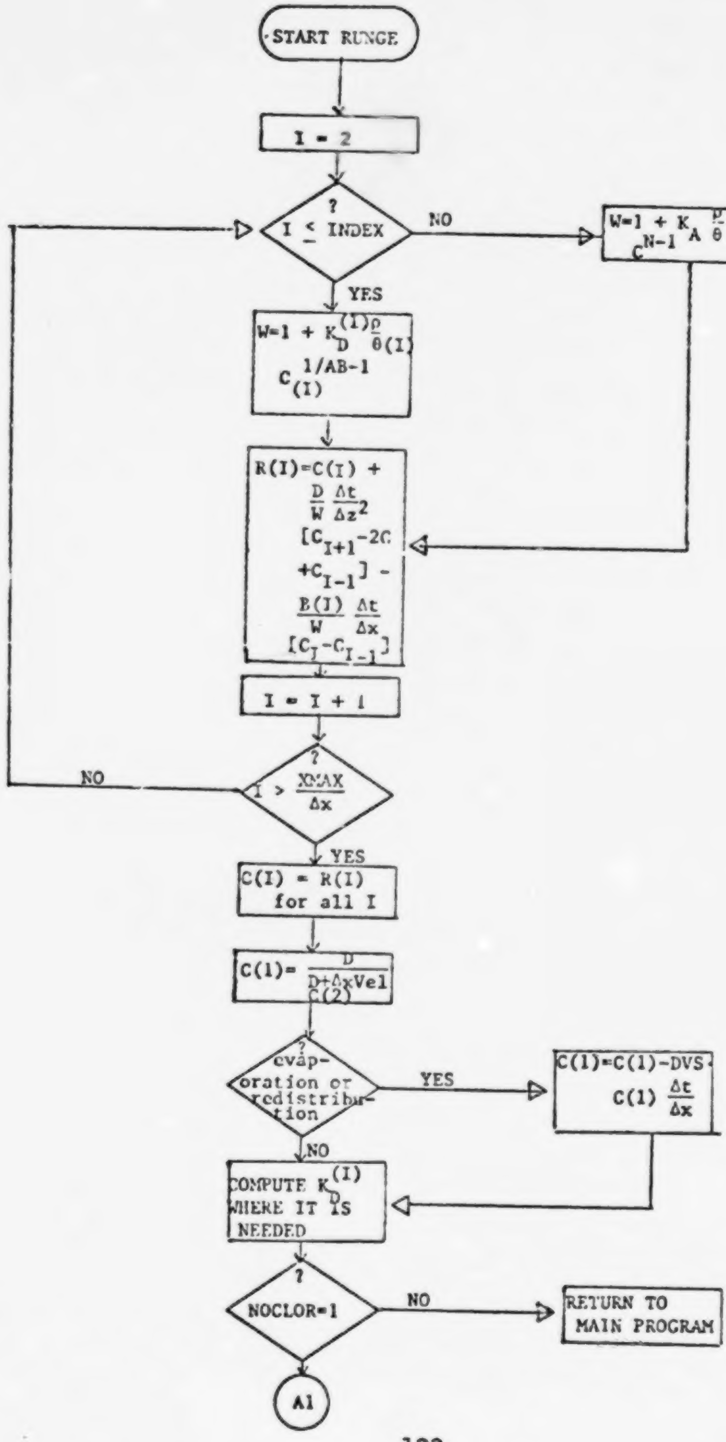

START
READ NTOTAL
?
NTOTAL=0
YES
STOP
1F
NO
CALL FLTRAT
READ N,NUMBER
NOREAD, NOCLOR
READ NAMEIT(J)
READ D,K,RHO,
T,NEXP
READ AB,CO,
PULSE,DVS
INITIALIZE
APPROPRIATE
VARIABLES
?
NOREAD
0
1 or 2
-1
C(1) = CO
C(J) = 0 FOR
ALL X
CONSTANT VALUE OF C(J)
BASED ON THETAX, K, N, AB,
CO, RHO.
0 < x < PULSE
?
NOREAD=1
NO
YES
READ C(J);
S(J)
READ C(J)
0 < x < PULSE
?
NOCLOR=1
NO
YES
READ CLORID(J)
?
N
0
1
READ DELTMT,
TTIMER
A1
READ DELT,
TMAX,X,STARTT
?
NOREAD = 0
YES
B1
NO
NVAL = 3
1D
1E

FLOW CHART FOR SIMULTANEOUS TRANSPORT OF WATER AND SOLUTE PROGRAM — MAIN PROGRAM (Continued)

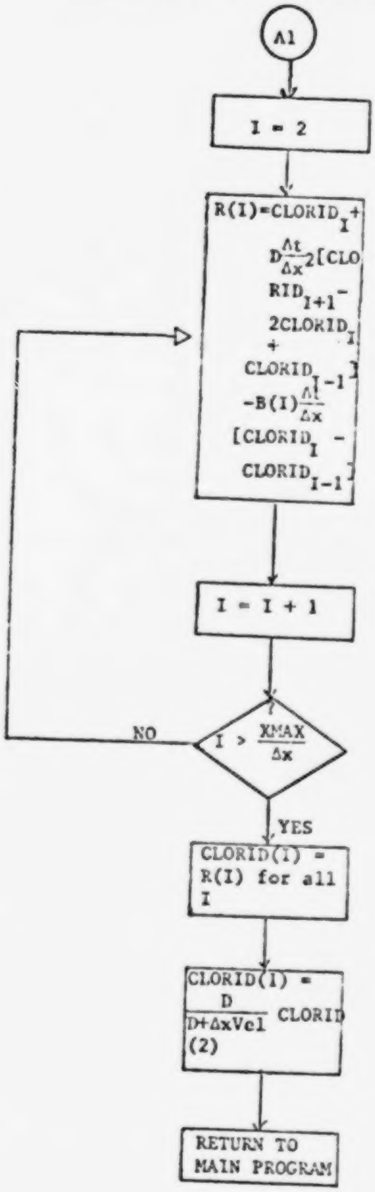


1C
NVAL = 2
DELX=DELXMT (NUMBER)
TIMER=TTIMER (NUMBER)
NUMBER=NUMBER-1
1E
A1
?
NOREAD=0
NO
YES
B1
B1
?
NOCLOR=1
YES
CLORID(1)=CO
NO
C(1) = CO
1B
CALL RUNGE
TIME = TIME + KTIME
1E
NO
WRITE C,S, CLORIDE TIME=STARTT Z=X POINT
YES
?
TIME=STARTT
3
?
NVAL
2
?
TIME=TIMER
YES
2B
NO
1E
1
STARTT=STARTT + DELT
?
C > T
YES
?
N
0
1C
1
1D
NO
?
STARTT<TMAX
YES
1E
1E
CALL FLTRAT
NO
NTOTAL=NTOTAL-1
1F
2B
WRITE C,S, CLORID VS X
?
NVAL
2,3
COMPUTE COEF. FOR RUNGE
1B
1
COMPUTE COEF. FOR RUNGE
B1
CALL SIMPSN
WRITE ∫C*θdx
1F
NTOTAL=NTOTAL-1
NO
?
NUMBER≥1
YES
1C

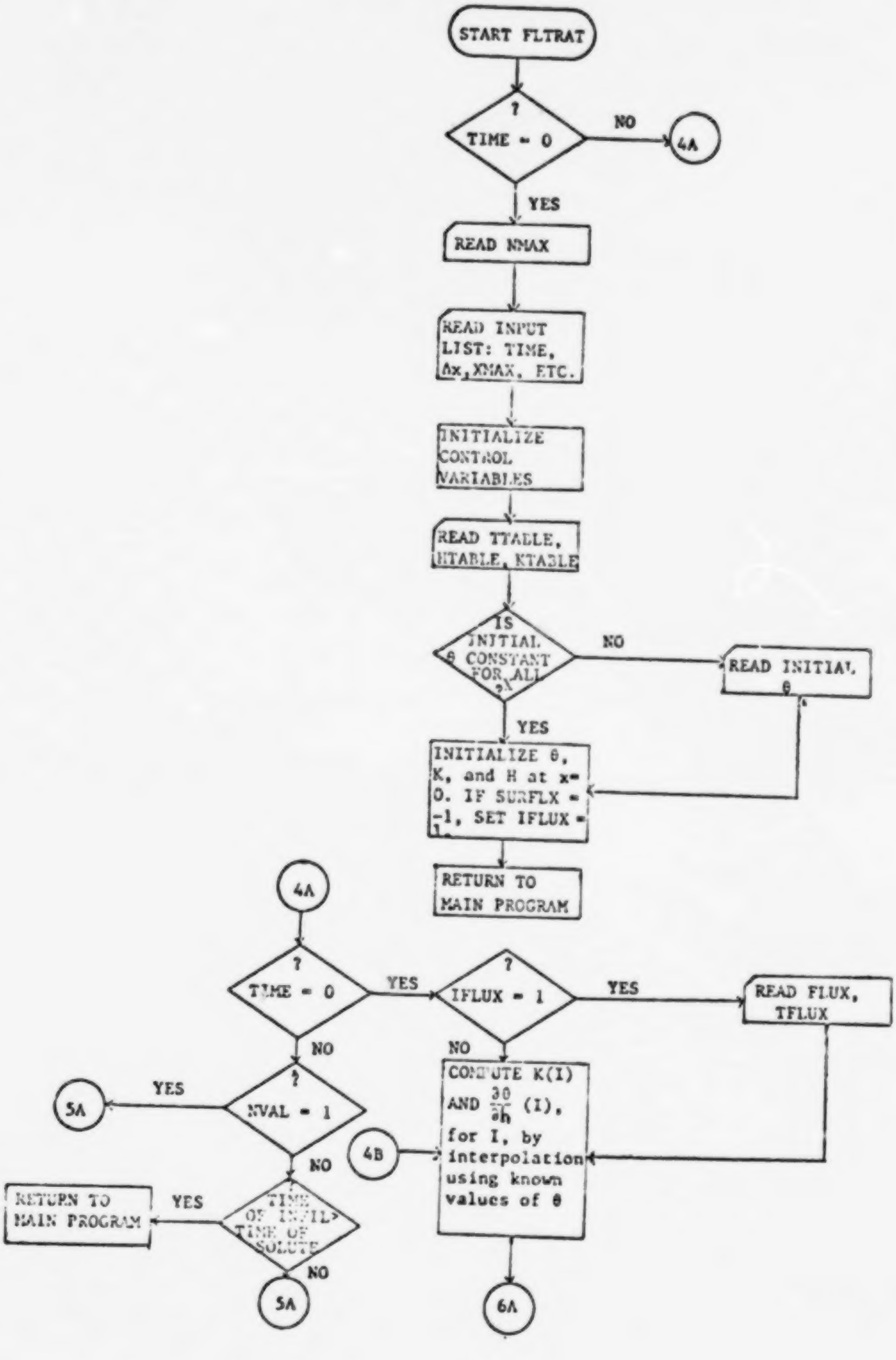
FLOW CHART FOR SIMULTANEOUS TRANSPORT OF WATER AND SOLUTE PROGRAM — RUNGE SUBROUTINE


START RUNGE
I = 2
?
I ≤ INDEX
NO
YES
W=1 + K_{C^{N-1}} A ρ/θ
W=1 + K_D^{(I)} ρ/θ(I) C_{(I)}^{1/AB-1}
R(I)=C(I) + D/W Δt/Δz² [C_{I+1}-2C +C_{I-1}] - B(I)/W Δt/Δx [C_I-C_{I-1}]
I = I + 1
?
I > XMAX/Δx
NO
YES
C(I) = R(I) for all I
C(1)= D/(D+ΔxVel) C(2)
?
evaporation or redistribution
YES
C(1)=C(1)-DVS· C(1) Δt/Δx
NO
COMPUTE K_D^{(I)} WHERE IT IS NEEDED
?
NOCLOR=1
NO
RETURN TO MAIN PROGRAM
A1

FLOW CHART FOR SIMULTANEOUS TRANSPORT OF WATER AND SOLUTE PROGRAM — RUNGE SUBROUTINE (Continued)

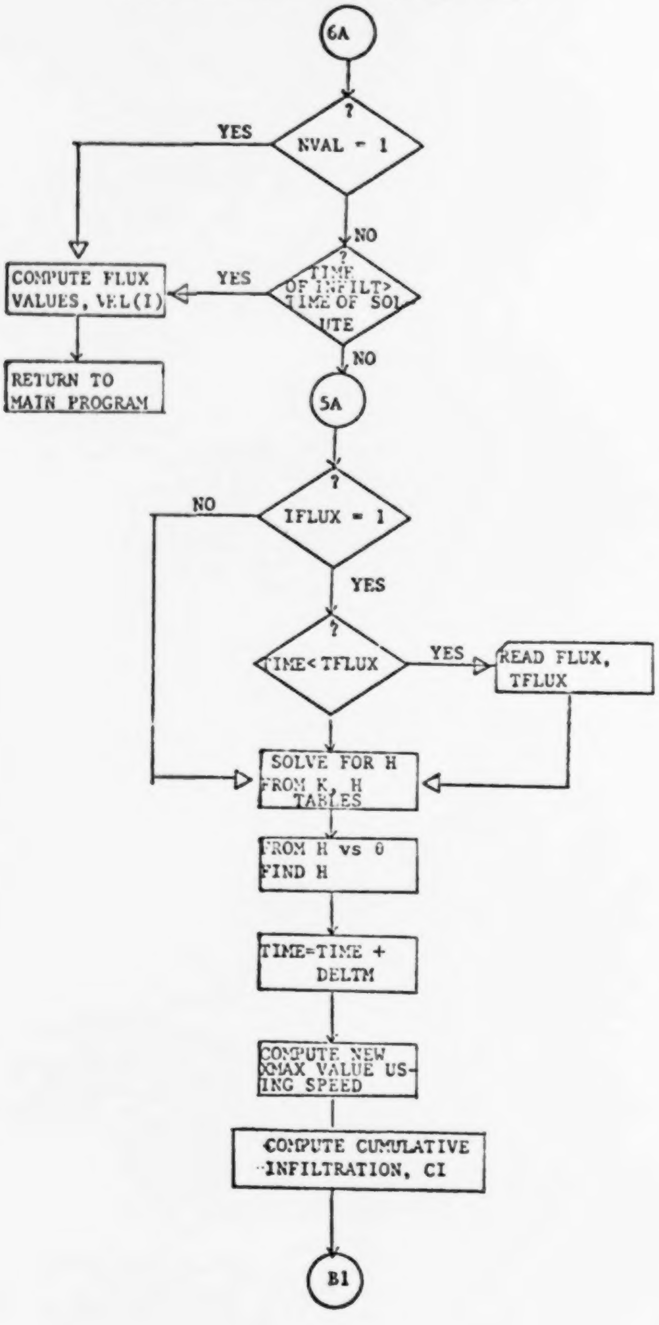

A1
I = 2
R(I)=CLORID$_I$+ $D\frac{\Delta t}{\Delta x^2}$[CLORID$_{I+1}$ − 2CLORID$_I$ + CLORID$_{I-1}$] −B(I)$\frac{\Delta t}{\Delta x}$ [CLORID$_I$ − CLORID$_{I-1}$]
I = I + 1
I > $\frac{XMAX}{\Delta x}$
NO
YES
CLORID(I) = R(I) for all I
CLORID(I) = $\frac{D}{D+\Delta x Vel}$ CLORID (2)
RETURN TO MAIN PROGRAM

FLOW CHART FOR SIMULTANEOUS TRANSPORT OF WATER AND SOLUTE PROGRAM — FLTRAT SUBROUTINE

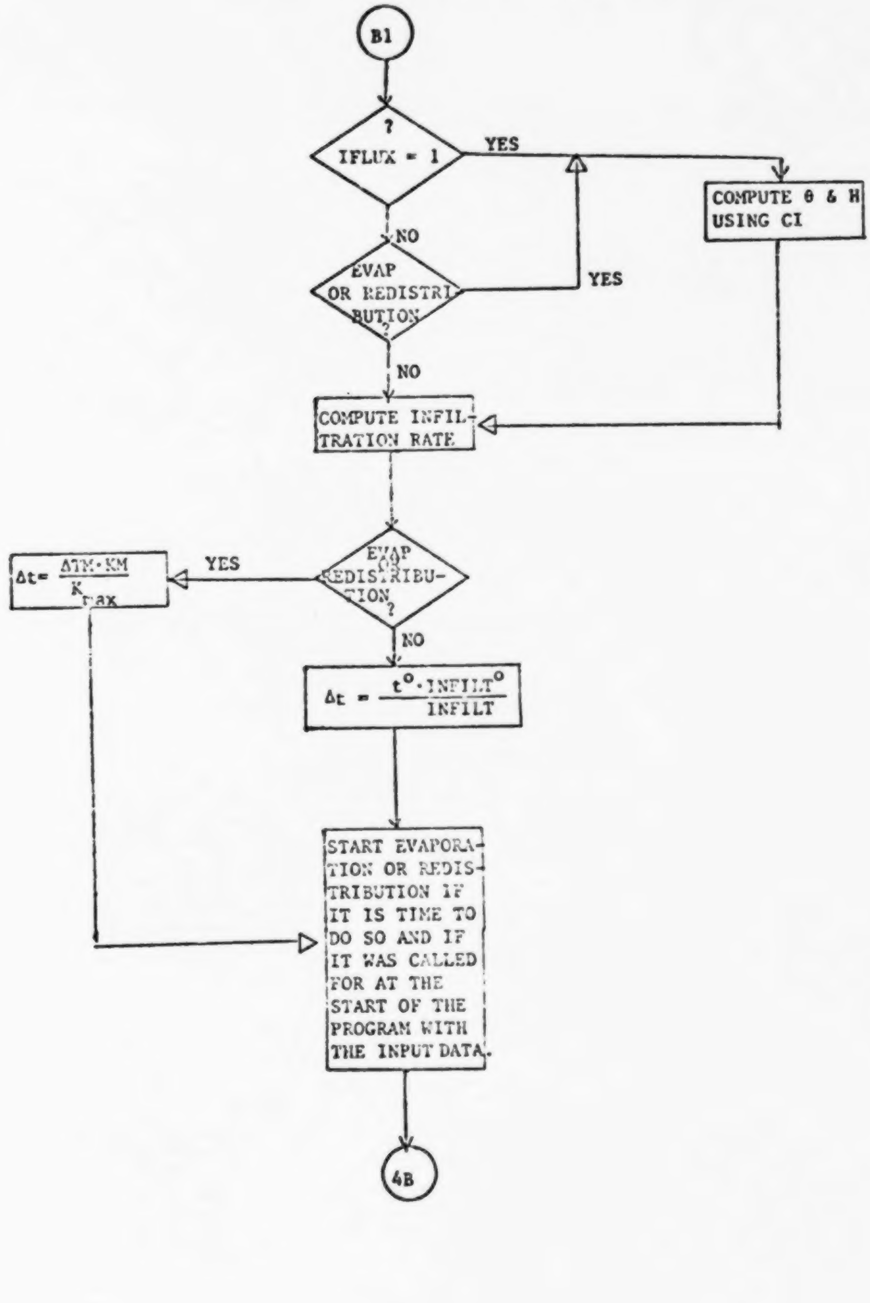


START FLTRAT
?
TIME = 0
NO
4A
YES
READ NMAX
READ INPUT LIST: TIME, Δx, XMAX, ETC.
INITIALIZE CONTROL VARIABLES
READ TTABLE, HTABLE, KTABLE
IS INITIAL θ CONSTANT FOR ALL x?
NO
READ INITIAL θ
YES
INITIALIZE θ, K, and H at x=0. IF SURFLX = -1, SET IFLUX = 1.
RETURN TO MAIN PROGRAM
4A
?
TIME = 0
YES
?
IFLUX = 1
YES
READ FLUX, TFLUX
NO
NO
COMPUTE K(I) AND $\frac{\partial\theta}{\partial h}$ (I), for I, by interpolation using known values of θ
4B
?
NVAL = 1
YES
5A
NO
TIME OF INFIL> TIME OF SOLUTE
YES
RETURN TO MAIN PROGRAM
NO
5A
6A

FLOW CHART FOR SIMULTANEOUS TRANSPORT OF WATER AND SOLUTE PROGRAM --- FLTRAT SUBROUTINE (Continued)


6A
?
NVAL = 1
YES
NO
?
TIME OF INFILT> TIME OF SOLUTE
YES
COMPUTE FLUX VALUES, VEL(I)
RETURN TO MAIN PROGRAM
NO
5A
?
IFLUX = 1
NO
YES
?
TIME< TFLUX
YES
READ FLUX, TFLUX
SOLVE FOR H FROM K, H TABLES
FROM H vs θ FIND H
TIME=TIME + DELTM
COMPUTE NEW XMAX VALUE USING SPEED
COMPUTE CUMULATIVE INFILTRATION, CI
B1

FLOW CHART FOR SIMULTANEOUS TRANSPORT OF WATER AND SOLUTE PROGRAM — FLTRAT SUBROUTINE (Continued)



B1
? IFLUX = 1
YES
NO
COMPUTE θ & H USING CI
EVAP OR REDISTRIBUTION ?
YES
NO
COMPUTE INFILTRATION RATE
EVAP OR REDISTRIBUTION ?
YES
$\Delta t = \frac{\Delta TM \cdot KM}{K_{max}}$
NO
$\Delta t = \frac{t^{o} \cdot INFILT^{o}}{INFILT}$
START EVAPORATION OR REDISTRIBUTION IF IT IS TIME TO DO SO AND IF IT WAS CALLED FOR AT THE START OF THE PROGRAM WITH THE INPUT DATA.
4B

SIMULTANEOUS TRANSPORT OF WATER AND SOLUTE PROGRAM

```
C
C     HYBRID PROGRAM-- SOLVES INFILTRATION AND SOLUTE EQUATIONS SIMUL-
C     TANEOUSLY.  THE MAIN PROGRAM IS THE CONTROL PROGRAM.
C
C     C= ABSOLUTE CONCENTRATION OF SOLUTE
C     S= SORBED VALUES
C     CLORID= THE CONDENTRATION OF CLORIDE WHENEVER A CLORIDE (K=0) CAL-
C     CULATION IS TO BE DONE SIMULTANEOUSLY WITH THE HERB- OR PEST-ICIDE
C     CALCULATIONS.
C     NEXP= THE CONSTANT EXPONENT ON THE TERM C**N, NEXP=N.
C     AB= THE CONSTANT IN THE EXPONENT ON THE TERM C**(1/AB) USED FOR
C           DESORPTION
C     VEL=VELOCITY
C     RHO= BULK DENSITY OF SOIL
C     THETA= VOLUMETRIC WATER CONTENT
C     K= THE CONSTANT K
C     D= DIFFUSION COEFFICIENT
C     DVS= CONSTANT DIFFUSION DOEFFICIENT FOR VAPOR PHASE OF C, USED FOR
C        INFILTRATION AND REDISTRIBUTION TO CALCULATE SURFACE FLUX OF
C        THE CHEMICAL.
C     CO= THE MAGNITUDE OF THE INPUT PULSE
C     KTIME= THE TIME INCREMENT USED IN THE CALCULATIONS.  THIS WILL BE
C        A CONSTANT FOR CONSTANT SURFACE FLUX RUNS, AND WILL BE A VARIA-
C        ABLE, DEPENDENT ON INFILTRATION RATE OR MAX CONDUCTIVITY FOR
C        PONDED INFILTRATION OR REDISTRIBUTION (OR EVAPORATION) RUNS.
C        NOT TO BE CONFUSED WITH DELT.
C     H= THE SPATIAL INCREMENT, SIMILAR IN USE TO KTIME, USUALLY EQUAL
C        TO .2, NOT TO BE CONFUSED WITH DELX.
C     T= THE AMOUNT OF CUMULATIVE INFILTRATION WHICH THE PROGRAM HAS TO
C        GENERATE WHILE PUTTING IN A PULSE OF CO AT THE SURFACE.  FOR
C        CUM INFILT < T, CO IS APPLIED AT THE SURFACE.
C     TMAX= THE MAXIMUM TIME UNDER STUDY THAT WATER IS TO BE APPLIED TO
C        THE SOIL SYSTEM.
C     DELT= INCREMENTAL TIME FOR WHICH SAMPLES ARE TO BE TAKEN.  FOR
C        EVERY DELT BETWEEN STARTT AND TMAX, A VALUE OF C WILL BE
C        PRINTED.
C     STARTT= THE STARTING TIME FOR THE BEGINNING OF THE DELT PRINT-
C        OUTS, USED ONLY FOR CONSTANT X RUNS, MUST BE GREATER THAN T.
C     XMAX= MAXIMUM DISTANCE INTO SOIL SURFACE, IN CM, MUST BE A  MULTI-
C        PLE OF H.
C     DELX= THE PRINTOUT X INCREMENT FOR C VS X PRINTOUT RUNS.  THE DELX
C        VALUES ARE ALL STORED IN THE MATRIX DELXMT.
C
C     THE PROGRAM WILL EITHER GENERATE CHEMICAL BY APPLYING IT AT A CON-
C        CENTRATION OF CO AT THE SURFACE, OR GENERATE AN INITIAL DISTRI-
C        BUTED PULSE AT TIME=0, OR ACCEPT INITIAL VALUES OF C AS SUPPLI-
C        ED ON CARDS; THE PARAMETER NOREAD DETERMINES THE PROCESS OF EN-
C        TERING THE CHEMICAL.
C
C     NOREAD: FOR EACH RUN:
C           IF NOREAD=0, DO NOT READ IN THE INITIAL S AND C VALUES
C           IF NOREAD=1, READ IN THE INITIAL S AND C VALUES, SET T=0,
C                        SPECIFY AN INTIIAL PULSE LENGTH.
C           IF NOREAD=-1, DO NOT READ IN THE INITIAL S AND C VALUES, SET
C                        T=0, SPECIFY INITIAL PULSE LENGTH
C
C     IF NOREAD=0, THE PROGRAM WILL PUT A PULSE IN UNTIL THE CUMULATIVE
C        INFILTRATION REACHES THE AMOUNT T.
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C     IF NOREAD =-1, THE PROGRAM WILL PUT IN ITS OWN INITIAL C VALUES,
C        COMPUTED FROM THE GIVEN PARAMETERS AND THETA INITIAL;, C=0 FOR
C        X>PULSE.
C     IF NOREAD=+1, YOU ARE TO READ IN ON CARDS, 8 VALUES OF (C INITIAL)
C        TO A CARD, A TOTAL OF 1+PULSE/H VALUES OF C.  THE PROGRAM WILL
C        ASSUME C=0 FOR X>PULSE.
C     IF NOREAD=+2, FOLLOW THE PROCEDURE OUTLINED FOR NOREAD=+1, EXCEPT
C        ALSO READ IN THE SAME NUMBER OF S VALUES.  THIS OPTION ALLOWS
C        THE COMPUTER TO ASSIGN KDES NUMBERS BASED ON S AND C, WHEREAS
C        FOR NOREAD=+1, ALL KDES VALUES ARE BASED ONLY UPON C AND CMAX.
C
C     NTOTAL= TOTAL NUMBER OF TIMES THE PROGRAM IS TO BE RUN.
C     N: FOR  EACH RUN, IF N=1, X IS HELD CONSTANT, TIME IS VARIED ON
C                       THE PRINTOUTS.
C                       IF N=0, TIME IS HELD CONSTANT, X IS VARIED ON
C                       THE PRINTOUTS.
C
C     NUMBER= TO BE USED ONLY FOR CONSTANT T RUNS.  THIS TELLS THE TOTAL
C        NUMBER OF DIFFERENT TIMES DURING THE RUN THAT THE X VALUES ARE
C        TO BE PRINTED OUT.
C
C     PULSE= THE DISTANCE IN THE SOIL OF THE LEADING EDGE OF AN INITIAL-
C        LY DISTRIBUTED CHEMICAL. MAKE SURE PULSE IS LARGE ENOUGH TO
C        COVER BOTH C AND CLORID DISTRIBUTIONS.
C
C     NOCLOR= FOR EACH RUN, IF NOCLOR=1, THEN THE PROGRAM WILL SIMULTANE-
C        OUSLY COMPUTE A CLORIDE RUN ALONG WITH THE REGULAR PESTICIDE
C        RUN, USING THE SAME PARAMETERS EXCEPT SETTING K=0.
C        IF NOCLOR=0, THE CLORIDE CALCULATIONS WILL NOT BE MADE.
C
C     TTIMER(J)= THE MATRIX WHICH STORES THE PRINTOUT TIMES FOR C VS X
C        PRINTOUT RUNS.
C
      REAL K,KTIME,NEXP,KRHO,KDES,KOND,INFILT
      DIMENSION C(802),S(802),THETA(802),VEL(802),B(802),DC(802),HJ(802)
     *,ZK1(802),KDES(802),CMAXUM(802),NAMEIT(20)
      DIMENSION VPAST(802),CLORID(802),TTIMER(200),DELXMT(200)
      COMMON /BLOK1/ C,S,DC/BLOK2/THETX,VEL,HJ,ZK1,XMAX/BLOK3/H,KTIME,L2,
     * LM2/BLOK4/ A,B,DENOM,INDEX,INDEX1,SMAX,ANT,AX       /BLOK5/THETA
     * /BLOK6/INFILT,CI,IISAVE,KUICK,TINCER/BLOK7/NOSTOP,DENAM
      COMMON /BLOK8/ IGOR,NVAL
      COMMON /BLOK9/ KDES,KLEW,DESKRO,XPONT,KLEW1
      COMMON /BLOK10/CMAXUM,DVST
      COMMON /BLOK11/TTIME
      COMMON /BLOK12/CLORID,NOCLOR
      READ(5,10) NTOTAL
  230 IF(NTOTAL .LE. 0) STOP
      NVAL=1
      INTGER= 0
      CI=0
      INFILT=0
      WRITE(6,999)
      CALL FLTRAT(INTGER,TIME,KOND,DAY,II,JJ,JXT,THETAT,I)
C
C     IF N=1, NUMBER NEED NOT BE SPECIFIED
C
      READ(5,10) N,NUMBER,NOREAD,NOCLOR
C
C     THE VARIABLE NAMEIT IS USED AS IDENTIFICATION. READ IN ON ONE CARD
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C     THE HEADING WHICH WILL BE PRINTED ON EVERY PRINTOUT.
C
      READ(5,104) (NAMEIT(J),J=1,20)
      READ(5,20) D,K,RHO,T,NEXP,AB,CO,PULSE,DVS
      DENOM=0
      DENAM=0
      A1= KOND/DAY/THETAT
      A2=T
      A4=D
      ABX= AB*NEXP
      KRHO= K
      NOSTOP=0
      DESKRO= KRHO/AB
      KLEW1=1
      THETA(II+1)= THETA(II)
      DO 1150 I=1,II
      VPAST(I)= 0
      CMAXUM(I)=0
 1150 KDES(I)= DESKRO
      KRHO= KRHO*NEXP
      AX= NEXP-1.
      ANT=1./AB-1.
      KUICK= 15
      XPONT=NEXP-1./AB
      MP=PULSE/H +1.+.1*H
      INDEX=2
      INDEX1=2
      D=  A4*DAY
      DVS= DVS*DAY
      ADKH= D/H/H
      DABSD= ABS(D)
      THETX= THETA(II)
      DXP= ABS(XPONT)
      IF(DXP .LT. 1.E-14) NOSTOP=1
      IF(DXP .LT. 1.E-60) XPONT= 1.E-60
      IF((ANT .LT. 1.E-60) .AND. (ANT  .GT. -1.E-60)) ANT= 1.E-60
      IF((AX  .LT. 1.E-60) .AND. (AX   .GT. -1.E-60)) AX = 1.E-60
      DO 380 J=1,II
      CLORID(J)=0
      S(J)= 0
  380 C(J)= 0
      IF(NOREAD) 595,320,600
  600 KUICK= PULSE/H+1.001
C
C     FOR NOREAD=+1 OR +2, READ IN A TOTAL OF 1+PULSE/H VALUES OF C.
C     THEN, IF NOCLOR=1, START ON A NEW CARD AND READ IN THE SAME NUMBER
C     OF CLORID VALUES.
C
      READ(5,580) (C(J),J=1,KUICK)
      IF(NOCLOR .EQ. 1) READ(5,580) (CLORID(J),J=1,KUICK)
C
C     IF NOREAD=+2, READ IN 1+PULSE/H VALUES OF S.  THIS WILL ALLOW THE
C     KDES VALUES TO BE COMPUTED BY THE PROGRAM.
C
      IF(NOREAD .NE. 2) GO TO 1200
      READ(5,580) (S(J),J=1,KUICK)
      KOUNT=0
      DO 1210 I=1,KUICK
      J=KUICK-I+1
      IF(KQUIT) 1220,1220,1230
 1220 THEK= S(J)/(C(J)**NEXP)
      IF((THEK .GT. 1.015*K) .OR. (THEK .LT. .985*K)) KQUIT=J
      IF(KQUIT .EQ. 0) GO TO 1210
 1230 CMAXUM(J)= CO
      KDES(J)= S(J)/AB/(C(J)**(1./AB))
 1210 CONTINUE
      IF(KQUIT .GT. 1) INDEX=KQUIT
      INDEX1= INDEX+1
      KLEW1= INDEX1
 1200 TIME=0
      GO TO 320
  595 DO 1120 I=1,MP
      XC= CO/THETA(I)
      BETA= RHO*K*(XC**(NEXP-1.))*THETA(I)**(NEXP-2.)
      CNST= 1./(1.+RHO*K/THETA(I))
      MEMORY=1
      Z= 1./CNST
  387 Z= 1.+BETA*Z**(1.-NEXP)
      CNST= 1./Z
      XY= CNST+BETA*CNST**NEXP
      IF(ABS(XY-1.00) .LT. .0005) GO TO 382
      IF(MEMORY .GE. 100) GO TO 383
      MEMORY= MEMGRY+1
      GO TO 387
  383 WRITE(6,388) K,NEXP,CO,RHO,THETA(I),CNST
      IF((CNST .GT. 1.00) .OR. (CNST .LT. 0.0)) GO TO 384
      WRITE (6,386)
      GO TO 382
  384 WRITE(6,391)
      STOP
  382 C(I)= CNST*CO
      CLORID(I)= CO
      CMAXUM(I)= C(I)
 1120 CONTINUE
      TIME=0
      NP=MP+1
      KUICK= NP+1
      IF(KUICK .LT. 15) KUICK= 15
      GO TO 320
C
C     COMPUTE SOME CONSTANTS TO BE USED IN SUBROUTINE RUNGE
C
  590 CMAXUM(1)= CO
      TIME=0
C
  420 IF(IGOR) 1130,1130,70
 1130 DO 390 J=2,II
      XTHET= (THETA(J+1)-THETA(J-1))/2./H
      DERIV= (VEL(J)-VPAST(J))/KTIME/THETA(J)
      VPAST(J)= VEL(J)
      VEL(J)= VEL(J)/THETA(J)
      GG= (-VEL(J)*VEL(J)/THETA(J)*XTHET-DERIV)*KTIME/2.
      ZZ= VEL(J)-D*XTHET/THETA(J)
      B(J)= (ZZ-GG)*KTIME/H
  390 DC(J)= RHO/THETA(J)
      VPAST(1)= VEL(1)
      VEL(1)= VEL(1)/THETA(1)
      DC(1)= RHO/THETA(1)
      A= ADKH*KTIME
      VAVGR= (VEL(1)+VEL(2))*.5
      DENOM= (D+.08*VAVGR)/(D+(.08+H)*VAVGR)
      DENAM= (DABSD+.08*VEL(II))/(DABSD+(H+.08)*VEL(II))
C
C     PUT THE PULSE OF CO IN FOR A TIME T
C
   70 C(1)= CO
      CLORID(1)= CO
  460 DVST= DVS*THETA(1)
      CALL RUNGE(II,KRHO)
      TIME= TIME + KTIME
      GO TO (480,490,500),NVAL
  480 IF(CI-T) 430,60,60
  490 IF(TIME-TIMER-KTIME) 430,160,160
  500 IF(TIME-STARTT-KTIME) 430,250,250
C
  430 CALL FLTRAT(INTGER,TIME,KOND,DAY,II,JJ,JXT,THETAT,I)
      GO TO (420,435,435),NVAL
C
  435 IF(IGOR) 1140,1140,460
 1140 DC(JJ)= RHO/THETA(JJ)
      DO 396 J=JXT,II
      XTHET= (THETA(J+1)-THETA(J-1))/2./H
      DERIV= (VEL(J)-VPAST(J))/KTIME/THETA(J)
      VPAST(J)= VEL(J)
      VEL(J)= VEL(J)/THETA(J)
      GG= (-VEL(J)*VEL(J)/THETA(J)*XTHET-DERIV)*KTIME/2.
      ZZ= VEL(J)-D*XTHET/THETA(J)
      B(J)= (ZZ-GG)*KTIME/H
  396 DC(J)= RHO/THETA(J)
      VPAST(1)= VEL(1)
      VEL(JJ)= VEL(JJ)/THETA(JJ)
      A= ADKH*KTIME
      VAVGR= (VEL(1)+VEL(2))*.5
      DENOM= (D+.08*VAVGR)/(D+(.08+H)*VAVGR)
      DENAM= (DABSD+.08*VEL(II))/(DABSD+(H+.08)*VEL(II))
      GO TO 460
C
   60 INDEX=2
      INDEX1=2
      TIME= TTIME
      IF(N) 120,120,110
C
C     IF N=1, READ IN DELT,TMAX,X,STARTT
C     IF N=0, READ IN A TOTAL OF NUMBER VALUES OF DELX,TIMER PAIRS IN
C        IN THE MATRICES DELXMT AND TTIMER.
C
  320 IF(N) 1250,1260,1250
 1250 READ(5,20) DELT,TMAX,X,STARTT
      IF(NOREAD .EQ. 0) GO TO 590
      GO TO 110
 1260 DO 1240 J=1,NUMBER
      JC= NUMBER-J+1
 1240 READ(5,20) DELXMT(JC),TTIMER(JC)
      IF(NOREAD .EQ. 0) GO TO 590
C
C     STATEMENT 120 IS FOR C VS X PRINTOUT RUNS
C
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```
  120 DELX= DELXMT(NUMBER)
      TIMER= TTIMER(NUMBER)
      NVAL =2
      INT=DELX/H+.01*H
      IF(INT .LE. 0) INT=1
      TIMER=TIMER/DAY
  140 NUMBER=NUMBER-1
  150 IF(TIME)435,435,430
  160 PVOL= A1*TIME/XMAX/DAY
C
C     WRITE OUT THE C AND S VS X VALUES
C
  125 WRITE(6,109) (NAMEIT(J),J=1,20)
      BTIME= DAY*KTIME
      WRITE(6,30) A1,A4,K,BTIME,THETAT,RHO,A2,CO,AB,NEXP
      DO 171 J=1,IISAVE
      IF(J .GE. INDEX) GO TO 363
      S(J)= KDES(J)*AB*C(J)**(1./AB)
      S(J)= S(J)*RHO
      GO TO 171
  363 S(J)= K*C(J)**NEXP
      S(J)= S(J)*RHO
  171 CONTINUE
      DO 170 J=1,IISAVE,INT
      IF(J .EQ. IISAVE) GO TO 180
  190 IF((C(J) .LE. 1.E-6) .AND. (THETA(J) .LE. 1.002*THETX)) GO TO 170
  180 X=J-1
  360 SS= S(J)/RHO
  370 X=H*X
      TIMM=TIME*DAY
      VELJJJ= VEL(J)/DAY
      IF(NOCLOR) 1180,1180,1190
 1190 WRITE(6,210) TIMM,X,PVOL,C(J),SS   ,VELJJJ,THETA(J),HJ(J),CLORID(J)
      GO TO 170
 1180 WRITE(6,210) TIMM,X,PVOL,C(J),SS   ,VELJJJ,THETA(J),HJ(J)
  170 CONTINUE
      TINKER= TINCER*DAY
      INFILT= INFILT/DAY
      WRITE(6,998) INFILT,CI,TINKER
C
C     COMPUTE AND PRINT OUT THE INTEGRALS OF C*THETA*DX AND RHO*S*DX.
C
      CALL SIMPSN(SUMS,SUMC,SUM,IISAVE,H,SUMCL)
      WRITE(6,82) SUMC,SUMS,SUM
      IF(NOCLOR .EQ. 1) WRITE(6,91) SUMCL
      WRITE(6,999)
      IF(NUMBER .GE. 1) GO TO 120
  220 NTOTAL =NTOTAL-1
      GO TO 230
C
C     STATEMENT 110 IS FOR CONSTANT X
C     X IS THE X VALUE AT WHICH THE SAMPLES ARE TO BE TAKEN
C
  110 WRITE(6,109) (NAMEIT(J),J=1,20)
      BTIME= DAY*KTIME
      WRITE(6,30) A1,D,K,BTIME,THETAT,RHO,T,CO,AB,NEXP
      NVAL=3
      STARTT=STARTT/DAY
      DELT=DELT/DAY
      TMAX=TMAX/DAY
      INT=X/H+1.
  240 IF(TIME) 435,435,430
C
C     WRITE OUT THE C AND S VS TIME VALUES
C
  250 IF(C(INT) .LT. 1.E-6) GO TO 260
  270 PVOL= A1*TIME/XMAX/DAY
      TIMM=TIME*DAY
      IF(INT .GE. INDEX) GO TO 1100
      SS= KDES(INT)*AB*C(INT)**(1./AB)
      GO TO 1110
 1100 SS= K*C(INT)**NEXP
 1110 VELINT= VEL(INT)/DAY
      IF(NOCLOR) 1170,1170,1160
 1170 WRITE(6,210) TIMM,X,PVOL,C(INT),SS,VELINT   ,THETA(INT),HJ(INT)
      GO TO 260
 1160 WRITE(6,210) TIMM,X,PVOL,C(INT),SS,VELINT,THETA(INT),HJ(INT)
     *,CLORID(INT)
  260 STARTT=STARTT+DELT
      IF(STARTT .LE. TMAX) GO TO 240
      TINKER= TINCER*DAY
      INFILT= INFILT/DAY
      WRITE(6,998) INFILT,CI,TINKER
      PVOL=0
      NTOTAL=NTOTAL-1
      WRITE(6,999)
      GO TO 230
  300 STOP
   10 FORMAT(6I5)
   20 FORMAT(5F15.5)
   30 FORMAT(19X,      'VEL=',F10.3,5X,'D=',F10.3,5X,'K=',F10.3,5X,
     *'KTIME=',E10.3,5X,'THETA=',F10.3,/19X,'RHO=',F10.3,5X,'T=',F10.3,
     *  5X,'CO=',F9.3,8X,'AB=',F10.3,6X,'NEXP=',F10.3,
     *///,T9 ,'TIME',T26,'X',T35,'PORE VOLUME',T54,'C       S=K*C**(N OR
     *1/AB)',T82,'VELOCITY',T99 ,'THETA',T109,'PRESSURE, H',' CLORIDE:K=
     *0')
   82 FORMAT(1X,'THE TOTAL AMOUNT OF CONCENTRATION, C, PRESENT IS, C*THE
     *TA=',T54,F11.4,/,1X,'THE TOTAL AMOUNT OF CONCENTRATION, S, PRESENT
     * IS, S*RHO=',  T64,F11.4,/,'+',T64,'___________',/,1X, 'THE SUM OF
     * S AND C IS, RHO*S + C*THETA=',  T64,F11.4)
   91 FORMAT(1X,/,1X,'THE AMOUNT OF CLORIDE CONCENTRATION PRESENT IS CLO
     *RIDE*THETA=',T64,F11.4)
  104 FORMAT(20A4)
  109 FORMAT(1X,T23,84('*'),/,1X,T23,'*',T25,20A4,1X,'*',/,1X,T23,84('*'
     *),/)
  210 FORMAT( 3X,2(F11.5,4X),F11.5,2E15.5,4X,2(F11.5,4X),F11.3,E12.5)
  386 FORMAT(5X,/,5X,'SINCE C/CO, AFTER 100 ITERATIONS, IS .GT. 0 AND .L
     *T. 1.0, THE CALCULATIONS WILL PROCEED USING THIS VALUE.',/)
  398 FORMAT(1X,/,5X,'FOR THE PARAMETERS: K=',F12.4,', NEXP=',F12.4,', C
     *O=',F12.4,', RHO=',F12.4,', THETA=',F12.4,//,5X,'AND FOR AN INITIA
     *LLY DISTRIBUTED PULSE, CONVERGENCE DID NOT OCCUR ON THE ITERATIVE'
     *,/,5X,'CALCULATIONS OF THE INITIAL C/CO AND S/CO VALUES. AFTER 100
     * ITERATIONS THE VALUE OF C/CO= ',E14.7,/)
  391 FORMAT(5X,/,5X,'THE CALCULATION OF C/CO IS OUTSIDE THE ALLOWED RAN
     *GE.',/,5X,'THEREFORE, YOU MUST READ IN THE VALUES OF C/CO AND S/CO
     * ON CARDS. THIS CAN BE DONE BY SETTING THE VALUE OF NOREAD=1',/)
  580 FORMAT(8F10.0)
  998 FORMAT(1X,/,1X,'FOR THE ABOVE, INFILTRATION RATE= ',F12.7,',  ###
     * CUMULATIVE INFILTRATION= ',F12.7,' INFILTRATION DELT, TINCER=',F1
     *2.7,/)
 999 FORMAT(1H1)
      END
      SUBROUTINE RUNGE(L,KRHO)
      REAL K,KRHO,KDES
      DIMENSION B(802),D(802),U(802),R(802),S(802),KDES(802),CMAXUM(802)
     * ,CLORID(802)
      COMMON /BLOK1/U,S,D/BLOK3/H,K,L2,LM2/BLOK4/A,B,DENOM,INDEX,
     * INDEX1,SMAX,ANT,AX/BLOK7/NOSTOP,DENAM
      COMMON /BLOK9/ KDES,KLEW,DESKRO,XPCNT,KLEW1
      COMMON /BLOK10/CMAXUM,DVS
      COMMON /BLOK12/CLORID,NOCLOR
      COMMON /BLOK13/IREDIS
C
C     CALCULATES NEW VALUES OF C/CO USING OLD VALUES FOR THE EXPRESSION
C     S=KADS*C**N. STATEMENTS UP TO 270 COMPUTE HERBICIDE OR PESTICIDE
C     CONCENTRATIONS, AND STATEMENTS 280 TO 260 COMPUTE CLORIDE CONCEN-
C     TRATIONS IF NOCLOR=1.
C
      CPAST= U(INDEX)
      R(1)= 0
      R(L)=  0
      DO 30 I=2,INDEX1
      IF(U(I)) 40,40,50
   40 R(I)=          A*(U(I-1)+U(I+1))+B(I)*U(I-1)
      GO TO 30
   50 C= 1.+KDES(I)*D(I)*U(I)**ANT
      E= B(I)/C
      C=A/C
      R(I)= U(I)+(C*(U(I-1)-2.*U(I)+U(I+1))-E*(U(I)-U(I-1)))
   30 CONTINUE
      DO 100 I=INDEX ,L2
      IF(U(I)) 10,10,20
   10 R(I)=          A*(U(I-1)+U(I+1))+B(I)*U(I-1)
      GO TO 100
   20 C= 1.+KRHO*D(I)*U(I)**AX
      E= B(I)/C
      C=A/C
      R(I)= U(I)+(C*(U(I-1)-2.*U(I)+U(I+1))-E*(U(I)-U(I-1)))
  100 CONTINUE
      DO 130 I=2,L2
      U(I)= ABS(R(I))
  130 CONTINUE
      U(1)= ABS(U(2)*DENOM)
      IF(IREDIS .EQ. 2) U(1)= U(1)-DVS*U(1)*K/H
      U(L)= ABS(U(L2)*DENAM)
      IF(NOSTOP .EQ. 1) GO TO 270
      CMAX=0
      DO 60 I=KLEW1,L2
      IF(CMAXUM(I) .LT. U(I)) CMAXUM(I)= U(I)
      IF(U(I)-CMAX) 60,60,110
  110 INDEX=I
      CMAX=U(I)
   60 CONTINUE
      INDEX1= INDEX+1
      IF(INDEX1 .GT. L2) NOSTOP=1
      IF(INDEX1 .GT. L2) INDEX1= INDEX
      IF((KLEW1 .LT. INDEX) .AND. (INDEX .GT. 2)) GO TO 150
      IF(CPAST .LT. U(INDEX)) GO TO 270
      INDEX= INDEX1
  150 NIDEX= INDEX-1
```

SIMULTANEOUS TRANSPORT OF WATER AND SOLUTE PROGRAM (Continued)

```
      DO 140 I= KLEW1,NIDEX
  140 KDES(I)= DESKRD*CMAXUM(I)**XPONT
      KLEW1= INDEX
  270 IF(NOCLOR .NE. 1) RETURN
      DO 280 I=2,L2
      R(I)= A*(CLORID(I+1)-2.*CLORID(I)+CLORID(I-1))-B(I)*(CLORID(I)-
     * CLORID(I-1))+CLORID(I)
  280 CONTINUE
      DO 250 I=2,L2
  250 CLORID(I)= R(I)
      CLORID(1)= CLORID(2)*DENOM
      CLORID(L)* CLORID(L2)*DENAM
  260 RETURN
      END
      SUBROUTINE SIMPSN(SUMS,SUMC,SUM,II,H,SUMCL)
      DIMENSION C(802),S(802),DCC(802),THETA(802),CLORID(802)
      COMMON /BLOK12/ CLORID,NOCLOR
      COMMON /BLOK1/C,S,DCC/BLOK5/THETA
C
C     INTEGRATES S/CO AND C/CO FOR OUTPUT VALUES FROM SUBROUTINE RUNGE.
C
      SUMCL=0
      SUMC=0.
      SUMS=0.
   40 DO 13 NODD=2,II
      IF(NODD-II) 50,13,13
   50 SUMS= SUMS+2.*S(NODD)
      SUMC= SUMC+2.*C(NODD)*THETA(NODD)
      SUMCL= SUMCL+2.*CLORID(NODD)* THETA(NODD)
   13 CONTINUE
      SUMS= H/2.*(SUMS+S(1)+S(II))
      SUMC= H/2.*(SUMC+C(1)*THETA(1)+C(II)*THETA(II))
      SUMCL=(SUMCL+CLORID(1)*THETA(1)+CLORID(II)*THETA(II))*H/2.
      SUM=SUMS+SUMC
      RETURN
      END
      SUBROUTINE FLTRAT(INTGER,TTIME,KOND,DAY,IIN,JJ,JXT,THETAT,INT)
C
C     PROGRAM FOR INFILTRATION, COMPUTES THETA(X,T)
C
C     THESAT=THE VALUE OF THETA AT SATURATION
C     THETAX= THETA(X,0) AT T=0, X>0
C     THETAT= THETA(0,T) AT X=0, T>0.  IF A CONSTANT FLUX IS SUPPLIED,
C        THEN THETAT IS THE MAX THETA THAT CAN OCCUR AT THE SURFACE AT
C       INFINITE TIME.
C     HNOUTO= H(0,T) AT X=0, T>0.  IF A CONSTANT FLUX IS SUPPLIED, THEN
C        HNOUTO IS THE MOST POSITIVE H THAT CAN OCCUR AT THE SURFACE AT
C        INFINITE TIME.  THE 'MOST POSITIVE' MAY STILL BE A NEGATIVE #.
C     HNOUTN= H(N,T) AT X=XMAX, T>0
C     THETAN= THETA(N,T) AT X=XMAX, T>0
C     THETAJ= THETA(I,J) AT X=I, T=J
C     THETA1= THETA(I,J-1) AT X=I, T=J-1
C     HJ= H(I,J) THE PRESSURE HEAD AT X=I, T=J
C
C     KOND= THE CONDUCTIVITY AT THETA(0,T) AND H(0,T).  IF A CONSTANT
C        FLUX IS SUPPLIED, KOND IS THE CONDUCTIVITY AT INFINITE TIME
C        AT THE SURFACE.
C     COND= THE SATURATED CONDUCTIVITY
C     KPLUS= K(I+1/2,J+1/2), THE CONDUCTIVITY, K, AT X=I+1/2, T=J+1/2
C     REDIST= THE INFILTRATION DEPTH AT WHICH FLUX=0 TO START REDISTRI-
C        BUTION.  IF CI > REDIST, THE FLUX=0.
C     FLUX= A CONSTANT STEP APPROXIMATION OF THE PORTION OF THE SURFACE
C        FLUX DISTRIBUTION LASTING UNTIL TIME=TFLUX.  FOR A CONSTANT
C        THETAT AT THE SURFACE, FLUX WILL NOT BE USED.
C     EVAPOR= THE SURFACE FLUX WHEN EVAPORATION IS IN PROGRESS.
C     TIMEVP= THE TIME AT WHICH EVAPORATION WILL COMMENCE.
C
      REAL KPLUS(802),KOND,INFILT,KTIME,KTABLE,KMAX
C
C     FOR EVAPORATION, IF YOU DESIRE TO BEGIN EVAPORATION BASED ON CI
C     (LIKE REDISTRIBUTION), THEN IT IS NECESSARY TO SPECIFY SOME ARBI-
C     TRARY VALUE OF TIMEVP AND ALSO A VALUE OF REDIST, SO THAT IF CI>
C     REDIST, EVAPORATION WILL COMMENCE.  WHEN THIS OPTION IS USED, THE
C     VALUE OF TIMEVP IS IGNORED.
C
C     TINC= THE TIME INCREMENT
C     INFILT= THE INFILTRATION RATE
C     CFILT= THE CUMULATIVE INFILTRATION
C     AJ, BJ, BJ, AFPH= VARIABLES USED IN THE GAUSS ELIMINATION SCHEME
C          TO CALCULATE THE NEXT HJ VALUES
C     HTABLE= THE SET OF H VALUES IN THE THETA VS H TABLE
C     TTABLE= THE SET OF THETA VALUES IN THE SAME TABLE
C     KTABLE= STORES CONDUCTIVITY VALUES FOR THE K VS THETA TABLE
C     DELX= THE X INCREMENTAL VALUE FOR THE INFILTRATION PART OF THE
C        HYBRID PROGRAM. THIS MUST BE GREATER THAN OR EQUAL TO H, THE X
C        INCREMENTAL VALUE FOR THE LINDSTROM PART OF THE PROGRAM. IF
C        DELX>H, THEN DELX MUST BE AN INTEGER MULTIPLE OF H.
C     XMAX= THE MAXIMUM X VALUE
C     NMAX= THE NUMBER OF TABULATED H (OR THETA) VALUES TO BE READ IN
C     SPEED= THE ESTIMATED VELOCITY, IN CM/HOUR, OF THE LEADING EDGE
C        OF THE WETTING FRONT.
C
      DIMENSION THETAJ(802),THETA1(802),CFILT(802),HJ(802),AJ(802)
C
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C
C     SURFLX= FOR THOSE RUNS WHICH REQUIRE A SPECIFIED FLUX DISTRIBUTION
C        AT THE SURFACE, SET SURFLX=-1.  FOR PONDED CASES, SET SURFLX=0.
C        WHEN SURFLX=-1, THE FOLLOWING PROCEDURE MUST BE FOLLOWED: FOL-
C        LOWING THE DELX, TIMER DATA CARDS WHICH ARE READ IN FROM THE
C        MAIN PROGRAM, PUNCH A DATA CARD ACCORDING TO THE FOLLOWING
C        READ STATEMENT: READ(5,20) FLUX,TFLUX    THIS WILL FORCE THE
C        PROGRAM TO APPLY A CONSTANT FLUX UNTIL TIME=TFLUX.  AT THIS
C        TIME, ANOTHER CARD WITH  FLUX,TFLUX  MAY BE READ IN TO ALLOW A
C        STEP LIKE PROGRESSION OF DIFFERENT FLUX VALUES TO BE APPLIED AT
C        THE SURFACE.  THE PROGRAM WILL DISCONTINUE THE FLUX APPLICATION
C        WHEN REDISTRIBUTION OR EVAPORATION IS ASKED FOR.  IT WILL HALT
C        EXECUTION WHEN TIME=THE LAST TFLUX SPECIFIED IF TFLUX<TIMER FI-
C        NAL; OR WILL HALT IF TIME>TTIME FINAL.
C
      DIMENSION BJ(802),DJ(802),AFPH(802),TTABLE(200),HTABLE(200),
     * CPT(802),ZK1(802),VEL(802),KTABLE(200)
      COMMON /BLOK2/THETAX,VEL,HJ,ZK1,XMAX/BLOK3/H    ,KTIME,II,J2
     * /BLOK5/THETAJ/BLOK6/INFILT,CI,IISAVE,KUICK,TINCER
      COMMON /BLOK8/ IGOR,NVAL
      COMMON /BLOK11/ TIME
      COMMON /BLOK13/IREDIS
C
C     SMALLT= FOR REDISTRIBUTION OR EVAPORATION, THETA AT THE SURFACE
C        WILL NEVER BE ALLOWED TO DROP BELOW THIS NUMBER, SMALLT.
C
C     TLIMIT= THE UPPER LIMIT TO BE PLACED ON TINCER.  IF NO UPPER LIMIT
C        IS DESIRED, LEAVE BLANK OR SET TO ZERO.
C
C     PULSE= FOR NONCONSTANT INITIAL THETA VALUES, PULSE IS THE DISTANCE
C        DOWN THE COLUMN, MEASURED FROM X=0, FOR WHICH INITIAL VALUES OF
C        THETA ARE TO BE READ IN ON CARDS.  FOR X>PULSE, ALL THETA
C        VALUES WILL BE SET TO THETAX.  READ IN A TOTAL OF 1+PULSE/DELX
C        VALUES OF THETA, 8 TO A CARD.
C
      IGOR=0
      IF(INTGER) 640,640,2010
  640 READ(5,10) NMAX
C
C     READ IN TINC IN UNITS OF HOURS
C
      READ(5,20)KTIME,THETAX,THETAT,HNOUTO,HNOUTN,THETAN,KOND,DELX,H,
     * XMAX,COND,THESAT,TINC,SPEED,SURFLX,REDIST,EVAPOR,TIMEVP,TLIMIT,
     * PULSE,SMALLT
      WRITE(6,25) DELX,COND,THETAX,THETAT,HNOUTO,HNOUTN,THETAN,KOND-
     * XMAX,THESAT,KTIME,TINC,H,SPEED
   25 FORMAT(1X,/,T5,'X INCREMENT, DELX=',T40,F12.7,T55,'SATURATION COND
     *UCTIVITY, COND=',   T90,F12.7,/,T5,'THETA(X,0), THETAX=',T40,F12.7
     *,T55,'THETA(0,T), THETAT=', T90,F12.7,/,T5,'H(0,T), HNOUTO=',T40,
     *F12.7,T55,'H(XMAX,T), HNOUTN=',T67,F15.7,/,T5,'THETA(XMAX,T), THET
     *AN=',T40,F12.7,T55,'SURFACE CONDUCTIVITY, KOND=',T90,F12.7,/,T5,'X
     *MAX=',T40,F12.7,T55,'SATURATION THETA, THESAT=',T90,F12.7,/,T5,'KT
     *IME=',T40,F12.7,T55,'DELT FOR INFILTRATION, TINC=',T90,F12.7,/,T5,
     *'X INCREMENT FOR HERBICIDE PURTION, H=',T43,F9.7,T55,'SPEED, OF EA
     *RLY INFILTRATION=',T90,F12.7,/)
      DAY= KTIME/.00900
      KTIME=.0090000000
      ISTEP= DELX/H+.01*H
      KSTEP= ISTEP+1
      N3STEP= 1+2*ISTEP
      IIN= XMAX/H+2.+.01*H
      IINEND= (IIN/ISTEP)*ISTEP+KSTEP
      IIN= IINEND
      II= IIN-1
      JTINC =-1
      CIPAST=0
      TLIMIT= TLIMIT/DAY
      TNPAST=0
      MFFT=0
      J2= II-1
      IIEND= IIN-ISTEP
      J2END= IIEND-ISTEP
      IISTOP= IIEND
      IDOWN= ISTEP-1
      IVIL=1
      J2SAVE= J2
      INSAVE= IIN
      IISAVE= II
      IREG=0
      IPOST= N3STEP
      IPOST1= N3STEP+ISTEP
      TINC= TINC/DAY
      TINCER= TINC
      IF(TLIMIT .LT. 1.E-50) TLIMIT= 1.E60
      KOND=KOND*DAY
      COND=COND*DAY
      SPEED= SPEED*DAY
      SUMT=0
      DIFFT= THESAT-THETAX
  740 JJ=1
      JXT=2
C
C     READ IN THE TTABLE AND HTABLE VALUES, 5 TO A CARD FOR EACH GROUP
C        START WITH THE SMALLEST VALUES FIRST.  ALSO READ IN THE KTABLE
C        VALUES, SMALLEST VALUE FIRST.
C
      NMAX=NMAX+1
      READ(5,20) (TTABLE(I), I=2,NMAX)
      READ(5,20) (HTABLE(I), I=2,NMAX)
      READ(5,20) (KTABLE(I), I=2,NMAX)
      DO 960 I=2,NMAX
  960 KTABLE(I)= KTABLE(I)*DAY
      KTABLE(1)= KTABLE(2)*.998
      KTABLE(NMAX+1)= KTABLE(NMAX)
      TTABLE(NMAX+1)= TTABLE(NMAX)
      HTABLE(NMAX+1)= HTABLE(NMAX)+.01
      HTABLE(1)= HTABLE(2)+.01*HTABLE(2)
      TTABLE(1)= TTABLE(2)*.998
      IFLUX=0
      HJ(IIN)= HNOUTN
      THETAJ(IIN)= THETAN
      THETA1(IIN)=THETAN
      G=2.*DELX
      TIME=0
      CTC= 1./2./DELX/DELX
      CFILT(1)= 1
      CFT(IIN)=1
      VEL(IIN)=0
      IPULSE=0
      DO 30 I=2,II
      VEL(I)=0
      HJ(I)= HNOUTN
      CFILT(I)= 1
      CFT(I)=1
      THETAJ(I)= THETAX
   30 CONTINUE
C
C     IF A VALUE OF PULSE HAS BEEN ENTERED, READ IN 1+PULSE/DELX INITIAL
C     VALUES OF THETA, 8 TO A CARD. IF DELX>H, THE PROGRAM WILL TAKE
C     CARE OF THE POINTS BETWEEN THE INFILTRATION DELX GRID POINTS.
C
      IF(PULSE .LT. 1.E-50) GO TO 2220
      IPULSE= 1.+PULSE/DELX+.1*DELX
      IPULSE= IPULSE+ISTEP
      READ(5,2230) (THETAJ(I),I=1,IPULSE,ISTEP)
      DO 2240 I=2,IPULSE
      DO 2250 ITB=2,NMAX
      IF(THETAJ(I) .LE. TTABLE(ITB)) GO TO 2260
 2250 CONTINUE
 2260 HJ(I)=HTABLE(ITB-1)+(THETAJ(I)-TTABLE(ITB-1))/(TTABLE(ITB)-TTABLE(
     *ITB-1))*(HTABLE(ITB)-HTABLE(ITB-1))
 2240 CONTINUE
 2220 DO 2275 I=2,II
 2275 THETAI(I)= THETAJ(I)
      THSAVE= THETAJ(KSTEP)
      HJSAVE= HJ(KSTEP)
  800 IF(SURFLX .GT. -1.E-7) GO TO 870
      IFLUX=1
      FLUXCI=0
      WRITE(6,804)       THETAT,HNOUTO
  804 FORMAT(5X,'THESE CALCULATIONS WILL BE DONE FOR A FLUX DISTRIBUTION
     * AT THE SURFACE.  THE DISTRIBUTION WILL',/,5X,'BE APPROXIMATED BY
     *CONSTANT STEP VALUES OF FLUX, EACH APPLIED UNTIL TIME=TFLUX.',/,5X
     *,'AT INFINITE TIME, THE THETA AND H VALUES WILL APPROACH',F12.7,'
     *AND',F13.7,' RESPECTIVELY.',/)
      THETAJ(1)= THETAX
      THETAI(1)= THETAX
      ITSUM= 1000
      HJ(1)= HNOUTN
      JTINC= 0
      GO TO 860
  870 WRITE(6,806) THETAT,HNOUTO
  806 FORMAT(5X,'THESE CALCULATIONS WILL BE DONE FOR A VARIABLE FLUX AT
     *THE SURFACE,',/,5X,'WITH A CONSTANT THETA=',F12.7,' AND A CONSTANT
     * H=',F13.7,' AT THE SURFACE.',/)
      HJ(1)= HNOUTO
      THETAJ(1)= THETAT
      THETAI(1)= THETAT
      KPLUS(1)= KOND
      VEL(1)= KOND
  807 FORMAT(5X,'WHEN THE INFILTRATION EQUALS',F12.7,' REDISTRIBUTION WI
     *LL COMMENCE.',/,5X,'AT WHICH TIME THE SURFACE FLUX WILL BE SET TO
     *ZERO.',/)
  860 IREDIS=0
      IF(ABS(EVAPOR) .GT. 1.E-7) GO TO 1000
      TIMEVP= 1.E50
      GO TO 1010
 1000 IF(REDIST .GT. 1.E-20) GO TO 2270
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SIMULTANEOUS TRANSPORT OF WATER AND SOLUTE PROGRAM (Continued)

```
      WRITE(6,1020) TIMEVP,EVAPOR,SMALLT
 1020 FORMAT(5X,'WHEN THE TIME EQUALS',F12.6,' EVAPORATION WILL START AT
     * THE SURFACE.',/,5X,'THE EVAPORATION RATE WILL BE A CONSTANT AND E
     *QUAL TO A VALUE OF',F13.6,' UNTIL',/,5X,'THETA AT THE SURFACE REAC
     *HES ITS LOWER LIMIT OF',F12.7,/)
      IREDIS=1
      TIMEVP= TIMEVP/DAY
      EVAPOR= EVAPOR*DAY
      GO TO 900
 2270 TIMEVP= 1.E50
      IREDIS=1
      WRITE(6,2280) REDIST,EVAPOR,SMALLT
 2280 FORMAT(5X,'WHEN THE INFILTRATION CI EQUALS',F12.7,' EVAPORATION WI
     *LL START AT THE SURFACE.',/,5X,'THE EVAPORATION RATE WILL BE EQUAL
     * TO',F13.6,' UNTIL THETA AT THE',/,5X,'SURFACE REACHES ITS LOWER L
     *IMIT OF',F12.7,/)
      EVAPOR= EVAPOR*DAY
      GO TO 47
 1010 IF(REDIST .GT. 1.E-7) IREDIS=1
      IF(IREDIS) 890,900,890
  890 WRITE(6,807) REDIST
      GO TO 47
  900 REDIST=1.E14
   47 CIZ=0
      DO 630 I=1,IINEND,ISTEP
      ZK1(I)= 1
  630 CIZ=CIZ+THETAJ(I)*DELX
      INTGER=1
      RETURN
C
C     STATEMENTS 40 THROUGH 50 COMPRISE THE INTERPOLATION SCHEME TO
C     COMPUTE THE NEXT INFILTRATION VALUES FROM THE THETA VS H TABLE
C
 2010 THETAJ(KSTEP)= THSAVE
      HJ(KSTEP)= HJSAVE
      IF(TIME) 42,42,2080
 2080 IF(NVAL .EQ. 1) GO TO 41
      IF((TIME+.001*TINC) .LE. TTIME) GO TO 41
      ICOR=1
      RETURN
C
C     READ IN THE FIRST STEP APPROXIMATION OF THE FLUX DISTRIBUTION,
C     FLUX, AND THE TIME, TFLUX, WHICH WILL END THE APPLICATION OF THIS
C     FLUX STEP.
C
   42 IF(IFLUX .EQ. 0) GO TO 40
      READ(5,20) FLUX,TFLUX
      WRITE(6,1280) FLUX
 1280 FORMAT(1X,/,5X,'AT TIME=0, THE FLUX=',F10.4,/)
      ETIME=0
      FLUX= FLUX*DAY
      TFLUX= TFLUX/DAY
      VEL(1)= FLUX
   40 N=1
 1110 KMAX=0
      DO 50 I=1,IIEND,ISTEP
      CFT(I)= CFILT(I)
      GO TO (80,70,60),N
   80 IL=2
```

```
      IR= NMAX/2
      IF(TTABLE(IR) - THETA1(I)) 100,110,90
  110 IL= IR-1
      GO TO 60
  100 IL=IR
      IR= NMAX
   90 IDIF= IR-IL
  130 J= IR-IDIF/2
      IF(TTABLE(J)-THETA1(I)) 160,150,140
  150 IR=J
      IL= IR-1
      GO TO 60
  160 IL=J
      GO TO 170
  140 IR=J
  170 IDIF= IR-IL
      IF(IDIF .NE. 1) GO TO 130
   60 IF(IL .GT. 1) GO TO 65
      IL=2
      IR=3
   65 CFILT(I)= (TTABLE(IR)-TTABLE(IL))/(HTABLE(IR)-HTABLE(IL))
  610 KPLUS(I)= KTABLE(IL)+(THETA1(I)-TTABLE(IL))/(TTABLE(IR)-
     * TTABLE(IL))*(KTABLE(IR)-KTABLE(IL))
      IF(KPLUS(I) .GT. KMAX) KMAX=KPLUS(I)
   70 IF(IL .GT. 1) GO TO 75
      IL=2
      IR=3
   75 IF(THETA1(I+ISTEP)-TTABLE(IR)) 180,120,190
  120 N=2
      CFILT(I+ISTEP)= CFILT(I)
  630 KPLUS(I+ISTEP)= KTABLE(IL)+(THETA1(I+ISTEP)-TTABLE(IL))/
     *(TTABLE(IR)-TTABLE(IL))*(KTABLE(IR)-KTABLE(IL))
      IF(KPLUS(I+ISTEP) .GT. KMAX) KMAX= KPLUS(I+ISTEP)
  820 GO TO 50
  180 IF(THETA1(I+ISTEP)-TTABLE(IL)) 200,210,120
  210 N=3
      IR=IL
      IL=IL-1
      GO TO 50
  200 IF(THETA1(I+ISTEP)-TTABLE(IL-1)) 220,210,210
  190 IF(THETA1(I+ISTEP) .GT. TTABLE(IR+1)) GO TO 220
  230 IL=IR
      IR=IR+1
      N=3
      GO TO 50
  220 N=1
   50 CONTINUE
      IF(TIME) 610,610,2070
  610 DO 620 I= KSTEP,IIEND,ISTEP
  620 CFT(I)= CFILT(I)
      KPLUS(IIN)= KPLUS(IIEND)
      IF(IPULSE .GT. 0) KUICK= IPULSE+ISTEP
      IF(KUICK .LT. (8*ISTEP)) KUICK= 8*ISTEP
      GO TO 41
 2070 IF(NVAL .EQ. 1) GO TO 1130
C
C     STATEMENTS 240 THROUGH 280 COMPUTE THE
C     NEXT H (PRESSURE) VALUES, USING THE GAUSS-ELIMINATION METHOD OF
C     REDUCING A MATRIX, THE MATRIX TO BE REDUCED CONSISTS OF THE ARRAYS
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C      AJ, BJ, DJ, ANC AFPH, ALL DEVLEOPED FROM EQ. 4 OF THE ARTICLE
C
  402 IF(IVIL) 1120,1120,1130
 1120 IF((TIME+.001*TINC) .GE. TTIME) GO TO 1130
   41 TC= TINCER*CTC
  240 DO 250 I=1,IINEND,ISTEP
  250 THETA1(I)= THETAJ(I)
      IF(IFLUX) 921,921,930
  930 DO 864 I=KSTEP,IIEND,ISTEP
      Y=I
  864 IF(KPLUS(I) .GT. KOND) KPLUS(I)= KOND-KOND*Y*KTABLE(2)*.001
C
C     FLUXCI= EXPECTED CI DUE TO ALL PREVIOUS FLUX DISTRIBUTIONS, EX-
C     CLUDING THE PRESENT FLUX STEP.
C
C     CHECK TO SEE WHETHER A NEW VALUE OF FLUX AND TFLUX IS REQUIRED TO
C     BE READ IN.  IF REQUIRED, THEN READ FLUX AND TFLUX.
C
      IF(TIME .LT. TFLUX) GO TO 921
      FLUXCI= FLUXCI+(TFLUX-ETIME)*FLUX
      ETIME= TFLUX
      READ(5,20) FLUX,TFLUX
      STIME= ETIME*DAY
      WRITE(6,1290) STIME,FLUX
 1290 FORMAT(1X,/,2X,'AT TIME=',E11.4,' THE FLUX WAS CHANGED TO FLUX=',F
     *10.4,/)
      FLUX= FLUX*DAY
      TFLUX= TFLUX/DAY
      VEL(1)= FLUX
C
C     COMPUTE THE MATRIX
C
  921 DO 260 I= KSTEP,IIEND,ISTEP
      RC= TC/(CFILT(I)+CFT(I))*2.0
      ZK1(I)= (KPLUS(I-ISTEP)+KPLUS(I))*.5
      ZK2    = (KPLUS(I+ISTEP)+KPLUS(I))*.5
      AJ(I)= -RC*ZK1(I)
      BJ(I)= RC*(ZK1(I)+ZK2)+1.
      DJ(I)= -RC*ZK2
      AFPH(I)= RC*((HJ(I-ISTEP)+G-HJ(I))*ZK1(I)-(HJ(I)+G-HJ(I+ISTEP))*
     * ZK2)+HJ(I)
  260 CONTINUE
      AFPH(KSTEP)= AFPH(KSTEP)-AJ(KSTEP)*HJ(1)
      AFPH(IIEND)= AFPH(IIEND)-DJ(IIEND)*HJ(IINEND)
C
C     REDUCE THE MATRIX
C
      DO 270 I=KSTEP,J2END,ISTEP
      CONST= -AJ(I+ISTEP)/BJ(I)
      BJ(I+ISTEP)= BJ(I+ISTEP)+CONST*DJ(I)
      AFPH(I+ISTEP)= AFPH(I+ISTEP)+CONST*AFPH(I)
  270 CONTINUE
C
C     SOLVE FOR H
C
      HJ(IIEND)= AFPH(IIEND)/BJ(IIEND)
      DO 280 I=KSTEP,J2END,ISTEP
      J= IIEND+1-I
      Y=J
      HJ(J)=(AFPH(J)-DJ(J)*HJ(J+ISTEP))/BJ(J)
      IF(HJ(J) .GT. HNOUTO) HJ(J)= HNOUTO-Y*DELX
  280 CONTINUE
      IF(HJ(1) .GT. HNOUTO) HJ(1)= HNOUTO
C
C     STATEMENTS 290 THROUGH 300 COMPUTE THE NEXT THETA VALUES BY USING
C     THE RECENTLY COMPUTED H VALUES TO SEARCH THROUGH THE TABLE AND
C     LINEARILY INTERPOLATE
C
  290 N=1
      DO 300 I=1,IIEND,ISTEP
      GO TO (310,320,330),N
  310 IL=2
      IR=NMAX/2
      IF(HTABLE(IR) .GT. HJ(I)) GO TO 340
  350 IL=IR
      IR=NMAX
  340 IDIF=IR-IL
  360 J=IR-IDIF/2
      IF(HTABLE(J)-HJ(I)) 390,380,370
  380 IR=J
      IL=IR-1
      THETAJ(I)= TTABLE(J)
      GO TO 320
  370 IR=J
      GO TO 400
  390 IL=J
  400 IDIF= IR-IL
      IF(IDIF .NE. 1) GO TO 360
  330 IF(IL .GT. 1) GO TO 335
      IL=2
      IR=3
  335 THETAJ(I)= TTABLE(IL)+(HJ(I)-HTABLE(IL))/(HTABLE(IR)-
     * HTABLE(IL))*(TTABLE(IR)-TTABLE(IL))
  320 IF(IL .GT. 1) GO TO 325
      IL=2
      IR=3
  325 IF(HJ(I+ISTEP)-HTABLE(IR)) 410,420,430
  420 N=2
      THETAJ(I+ISTEP)= TTABLE(IR)
      GO TO 300
  430 IF(HJ(I+ISTEP) .LE. HTABLE(IR+1)) GO TO 440
  450 N=1
      GO TO 300
  440 IL=IR
      IR=IR+1
  480 N=3
      GO TO 300
  410 IF(HJ(I+ISTEP)-HTABLE(IL)) 460,470,480
  470 IR=IL
      IL=IL-1
      GO TO 420
  460 IF(HJ(I+ISTEP)-HTABLE(IL-1)) 450,490,500
  490 IR=IR-2
      IL=IL-2
      GO TO 420
  500 IR=IL
      IL=IL-1
      N=3
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SIMULTANEOUS TRANSPORT OF WATER AND SOLUTE PROGRAM (Continued)

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  300 CONTINUE
C
C     STATEMENTS 510 THROUGH 600 COMPUTE THE INFILTRATION, CHECK THE
C     PRINTOUT CONDITIONS AND STOP CONDITIONS, AND REINITIALIZE THETA1
C     AND KPLUS FOR ANOTHER ITERATION
C
  510 TIME=TIME+TINCER
  850 IF(IREG .EQ. 1) GO TO 530
      INOT= SPEED*TIME/H
      IIN= KUICK+INOT
      IINEND= (IIN/ISTEP)*ISTEP+KSTEP
      IIN= IINEND
      IF(IIN .GE. INSAVE) GO TO 872
      II= IIN-1
      J2= II-1
      IIEND= IINEND-ISTEP
      J2END= IIEND-ISTEP
      GO TO 530
  872 IREG=1
      IIN= INSAVE
      II= IISAVE
      J2= J2SAVE
      IINEND= IIN
      IIEND= IIN-ISTEP
      J2END= IIEND-ISTEP
  530 B=TIME/(TIME+3.3333333)
      IF(B .LT. .7) B=.7
      CI=0
      DO 550 I=JJ,IPOST,ISTEP
  550 CI=CI+DELX*THETAJ(I)
      CIPOST=0
      DO 2150 I=IPOST1,INSAVE,ISTEP
 2150 CIPOST= CIPOST+DELX*THETAJ(I)
      CI= CI-CIZ+CIPOST
      IF((IFLUX .NE. 1) .AND. (IREDIS .NE. 2)) GO TO 2020
      THETA2= THETAJ(1)
      IF(IFLUX .EQ. 1) GO TO 2040
      THETAJ(1)= THETAJ(1)+(CIEVAP+EVAPOR*(TIME-TIMERO)-CI)/DELX
      GO TO 2030
 2040 THETAJ(1)= THETAJ(1)+((TIME-ETIME)*FLUX+FLUXCI-CI)/DELX
 2030 IF(THETAJ(1) .LT. SMALLT) THETAJ(1)= SMALLT
      DO 950 I=2,NMAX
      IF(TTABLE(I) .GE. THETAJ(1)) GO TO 955
  950 CONTINUE
  955 ITB= I-1
      HJ(1)= HTABLE(ITB)+(THETAJ(1)-TTABLE(ITB))/(TTABLE(I)-TTABLE(ITB))
     * *(HTABLE(I)-HTABLE(ITB))
      CI= CI+THETAJ(1)-THETA2
 2020 DO 540 I=1,IINEND,ISTEP
      THETA1(I)= (THETAJ(I)-THETA1(I))*B+THETAJ(I)
  540 CONTINUE
      INFILT= (CI-CIPAST)/TINCER
      CIPAST= CI
      IF(IFLUX .EQ. 1) GO TO 1190
 1160 IF(JTINC) 1080,1040,1030
 1030 JTINC=0
      RATIO= TINC*INFILT
 1040 IF((IFLUX .NE. 1) .AND. (IREDIS .NE. 2)) GO TO 1050
 1060 IF(MFFT .EQ. 1) GO TO 1070
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      TINCER= RATIO/(CIPOST-PASTCI)
 2170 PASTCI=CIPOST
      TANCER= CONMAX/KMAX
      IF(TANCER .GT. TINCER) TINCER=TANCER
      IF(TINCER .GE. TLIMIT) MFFT=1
      IF(TINCER .GT. TLIMIT) TINCER= TLIMIT
      IF(TINCER .LT. TNPAST) TINCER= TNPAST
      TNPAST= TINCER
      GO TO 1070
 1080 JTINC= JTINC+2
      GO TO 1070
 1050 TINCER= RATIO/INFILT
 1070 CONTINUE
 1190 IF(IREDIS-1) 40,911,40
  911 IF((REDIST .LE. CI) .OR. (TIME .GE. TIMEVP)) IREDIS=2
      IF(IREDIS-2) 40 ,913,913
  913 FLUX=0
      IFLUX=0
      JTINC=0
      CIEVAP= CI
      TIMERD= TIME
      I= IIEND.
      DKTIME= KMAX*KTIME
      TIMP= TIME*DAY
      WRITE(6,2300) TIMP,CI
      CONMAX= KMAX*TINCER
      DMEDAN=.5*(THETAT-THETAX)+THETAX
 2190 IF(THETAJ(I) .GE. DMEDAN) GO TO 2200
      I=I-ISTEP
      GO TO 2190
 2200 IPOST1=I
      IPOST=I-ISTEP
      PASTCI=0
      CIPOST=0
      DO 2210 I=IPOST1,INSAVE,ISTEP
      PASTCI= PASTCI+DELX*THETAJ(I)
 2210 CIPOST=(THETAJ(I)-(THETA1(I)-THETAJ(I))/B)*DELX+CIPOST
      RATIO=(PASTCI-CIPOST)*TINCER
      GO TO 40
 1130 VEL(1)=     (-KPLUS(1)*((HJ(KSTEP)-HJ(1))/DELX-1.0))
      SUMT=       CI/DIFFT
      HJSAVE= HJ(KSTEP)
      THSAVE= THETAJ(KSTEP)
      MSTEP= KSTEP
      VEL(MSTEP)=     (-KPLUS(MSTEP)*((HJ(MSTEP)-HJ(1))/DELX-1.0))
      VELSAV= VEL(MSTEP)
      DO 660 I=1,IISTOP,ISTEP
      IF(I .EQ. 1) GO TO 2000
      MSTEP= I
      VEL(MSTEP)=     (-KPLUS(MSTEP)*((HJ(MSTEP)-HJ(I-ISTEP))/DELX-1.0))
 2000 IF((NVAL .EQ. 1) .AND. (I .LE. KSTEP)) GO TO 2050
      IF(I .EQ. N3STEP) VEL(MSTEP)= -KPLUS(MSTEP)*((HJ(MSTEP)-HJSAVE)/
     * DELX-1.0)
      IF((IREDIS .EQ. 2) .AND. (I .LE. KSTEP)) GO TO 2310
      GO TO 2060
 2310 IF(VEL(1) .LT. EVAPOR) VEL(1)= EVAPCR
      IF(VEL(KSTEP) .LT. EVAPOR) VEL(KSTEP)= EVAPOR
      GO TO 2060
 2050 IF(IFLUX .NE. 1) GO TO 2130
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SIMULTANEOUS TRANSPORT OF WATER AND SOLUTE PROGRAM (Continued)

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      VEL(MSTEP)= VEL(1)
      GO TO 2140
 2130 VEL(MSTEP)= .5*(VEL(1)+VELSAV)
      HJ(MSTEP)= .5*(HJ(1)+HJSAVE)
      THETAJ(MSTEP)= .5*(THETAJ(1)+THSAVE)
      ITSUM= SUMT/H+4.
 2140 DO 2110 JMP=1,IDOWN
      ITRATE= I+JMP
      IF(ITRATE .GT. ITSUM) GO TO 2120
      HJ(ITRATE)= HJ(MSTEP)
      VEL(ITRATE)= VEL(MSTEP)
      THETAJ(ITRATE)= THETAJ(MSTEP)
 2110 CONTINUE
      GO TO 660
 2060 IF(ISTEP-1) 660,660,970
  970 DO 930 JMP=1,IDOWN
      HJ(I+JMP)= HJ(MSTEP)
      VEL(I+JMP)= VEL(MSTEP)
      THETAJ(I+JMP)= THETAJ(MSTEP)
  930 CONTINUE
  660 CONTINUE
 2120 IF(NVAL .NE. 1) GO TO 2090
      KTIME= TINCER
      GO TO 2100
 2090 IF(IREDIS .NE. 2) KTIME= .009*KOND/VEL(1)
      IF(IREDIS .EQ. 2) KTIME= DKTIME/KMAX
      IF(KTIME .GT. .009) KTIME=.009
 2100 IF(IVIL) 1140,1140,1150
 1150 IVIL=0
      TTIME= KTIME
      IF(NVAL .EQ. 1) TTIME= TINCER
      TIME= TINCER
      IF(IFLUX .EQ. 1) GO TO 1120
 1140 RETURN
   10 FORMAT(3I5)
   20 FORMAT(5F15.5)
 2230 FORMAT(8F10.3)
 2300 FORMAT(1X,//,5X,'INFILTRATION CEASED AT TIME=',F15.5,' AND CUMULAT
     *IVE INFILTRATION=',F15.6,//)
      END
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